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**SUBSURFACE TRANSPORT OF HYDROCARBON FUEL
ADDITIVES AND A DENSE CHLORINATED SOLVENT**

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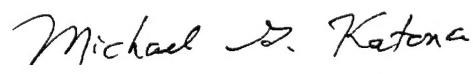
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PREFACE

This report was prepared by Auburn University, 202 Samford Hall, Auburn University, Alabama 36849, for the Armstrong Laboratory, Headquarters Air Force Civil Engineering Support Agency, Environics Directorate (AL/EQ), 139 Barnes Drive, Suite 2, Tyndall Air Force Base, Florida, 32403-5323, under contract F08635-93-C-0071.

This interim report describes the work done at Auburn University during the first year of the research project "Subsurface Transport of Hydrocarbon Fuel Additives and a Chlorinated Solvent." The project is focused on the subsurface environmental behavior of quadricyclane, which is a light nonaqueous-phase liquid (LNAPL) cyclic hydrocarbon fuel additive, and on the behavior of tetrachloroethylene (or, perchloroethylene), which is a dense nonaqueous-phase liquid (DNAPL) chlorinated hydrocarbon solvent.

The authors wish to thank Dr. B.F. Hajek, who assisted with the selection, collection, and characterization of the field soil samples, Mr. B.C. Missildine who assisted with the design and construction of some of the experimental equipment and with the performance of some of the experiments, Ms. J. Szechi who assisted with the chemical analyses and Ms. S.L. Davis who typed the report.

This project started on July 1, 1993. This interim report describes the work carried out between July 1, 1993 and June 30, 1994. The AL/EQ project officer was Capt. Thomas P. DeVenoge. Dr. Thomas B. Stauffer provided technical guidance through various stages of the work.

EXECUTIVE SUMMARY

A. OBJECTIVE

The purpose of this report is to describe the work carried out at Auburn University during the first year of the research project "Subsurface Transport of Hydrocarbon Fuel Additives and a Chlorinated Solvent", supported by the Armstrong Laboratory, Headquarters Air Force Civil Engineering Support Agency, Environics Division, under contract F08635-93-C0071.

B. BACKGROUND

This project is focused on the subsurface environmental behavior of quadricyclane, which is a light nonaqueous-phase liquid (LNAPL) cyclic hydrocarbon fuel additive, and on the behavior of tetrachloroethylene, or, as it is also called, perchloroethylene (PCE), which is a dense nonaqueous-phase liquid (DNAPL) chlorinated hydrocarbon solvent. There is very little information available on the subsurface chemical reactions and transport behavior of quadricyclane. This project includes a literature review on quadricyclane chemistry and physical properties, and a series of laboratory experiments in batch reactors, soil columns and a flow container to improve the present understanding of quadricyclane chemistry and transport behavior in four selected field soils. Regarding the subsurface transport behavior of perchloroethylene (PCE), the project includes a number of detailed laboratory experiments in flow columns and flow containers, utilizing a unique dual-energy gamma radiation system to measure water and PCE saturations, to provide detailed quantitative data sets on the multiphase transport of PCE in homogeneous and heterogeneous porous media. Such detailed quantitative data sets are presently lacking.

Various tasks have been defined as part of the project and a number of these tasks have been completed during the first year. The tasks that have been completed during the first year include a literature review on the properties of quadricyclane (namely, Task 1.1), the collection and characterization of a set of field soil samples for use in tests with quadricyclane (Task 1.2), initial chemical characterization of quadricyclane (Task 1.3), one-dimensional (1-D) transport experiments with PCE in laboratory columns with homogeneous porous media (Task 2.1), and the design and construction of a laboratory flow container for performing two-dimensional (2-D) transport experiments with PCE and quadricyclane (Task 2.2). In addition to these completed tasks, work has been initiated and is continuing on a number of other tasks, including laboratory batch and column experiments with quadricyclane and test soils (Task 1.4) and 1-D transport experiments with PCE in laboratory columns with heterogeneous porous media (Task 2.3). Although not yet initiated, a series of 2-D transport experiments will be performed during the second year of the study with quadricyclane (Task 1.5) and with PCE (Task 2.4) in laboratory flow containers packed with porous media, and most of the preparatory work necessary for the initiation of these tasks has been completed.

C. SCOPE

This report is organized into several sections each devoted to a particular task. For convenience, the literature references for each section are listed at the end of the particular section. Section I provides an introduction. Section II contains the literature review on properties of quadricyclane. Section III presents the laboratory chemical analyses of quadricyclane and its reaction products. Section IV describes the collection and analysis of the test soils. Section V presents the batch

experiments with quadricyclane and test soils, and Section VI is devoted to the 1-D column experiments with PCE. Section VII describes the experimental setup for the 2-D flow container experiments. Finally, the conclusions are presented in Section VIII.

D. CONCLUSIONS

This report describes the work performed during the first year of this project. The project is on schedule and there are no current or anticipated problems. All the tasks planned for the first year have been completed, and the preparatory work necessary for the initiation and performance of the remaining tasks has been either completed or is very close to completion. During the second year, work will be initiated on the planned 2-D transport experiments with quadricyclane and PCE (namely, Tasks 1.5 and 2.4). In addition, work will continue on additional batch and 1-D transport experiments with quadricyclane and test soils (Task 1.4), and on additional 1-D transport experiments with PCE with heterogeneous porous media (Task 2.3).

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SECTION I INTRODUCTION

A. OBJECTIVE

The objective of this report is to provide a description of the work done at Auburn University during the first year of the research project entitled "Subsurface Transport of Hydrocarbon Fuel Additives and a Dense Chlorinated Solvent", sponsored by the Environics Division of the Headquarters Air Force Civil Engineering Support Agency under contract F08635-93-C-0071. The project was initiated on July 1, 1993.

B. BACKGROUND

The project is focused on the subsurface environmental behavior of quadricyclane, which is a light nonaqueous phase liquid (LNAPL) cyclic hydrocarbon fuel additive, and on the behavior of tetrachloroethylene, or, as it is also called, perchloroethylene (PCE), which is a dense nonaqueous phase liquid (DNAPL) chlorinated hydrocarbon solvent. Various tasks have been defined as part of the project and a number of these tasks have been completed during the first year. The tasks that have been completed during the first year include a literature review on the properties of quadricyclane (namely, Task 1.1), the collection and characterization of a set of field soil samples for use in tests with quadricyclane (Task 1.2), initial chemical characterization of quadricyclane (Task 1.3), one-dimensional (1-D) transport experiments with PCE in laboratory columns with homogeneous porous media (Task 2.1), and the design and construction of a laboratory flow container for performing two-dimensional (2-D) transport experiments with PCE and quadricyclane (Task 2.2). In addition to these completed tasks, work has been initiated and is continuing on a number of other tasks, including laboratory batch and column experiments with quadricyclane and test soils (Task 1.4) and 1-D transport experiments with PCE in laboratory columns with heterogeneous porous media (Task 2.3). Although not yet initiated, a series of 2-D transport experiments will be performed during the second year of the study with quadricyclane (Task 1.5) and with PCE (Task 2.4) in laboratory flow containers packed with porous media, and most of the preparatory work necessary for the initiation of these tasks has been completed.

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SECTION II
LITERATURE REVIEW ON PROPERTIES
OF QUADRICYCLANE

A. INTRODUCTION

This section presents a review of the literature on the properties of quadricyclane and on its possible reactions in the subsurface environment.

The literature search for publications was divided into two parts. Initially, an extensive bibliography on quadricyclane was obtained, using the Chemical Abstract Service of the American Chemical Society. This information was used to investigate possible chemical reactions of quadricyclane. Additional information was obtained from the Applied Science and Technology Index, the Biological and Agricultural Index and the General Science Index. These references, however, provided no information on the behavior of quadricyclane in the soil environment. Subsequently, we concluded from the literature that quadricyclane behaves as a nonaqueous phase liquid (NAPL). Therefore, several reviews on NAPLs like those by Mercer and Cohen (1990), Cohen and Mercer (1993), Mackay et al. (1985), Huling and Weaver (1991) were employed to identify important parameters concerning the fate of NAPLs in the subsurface. The collected literature was then searched for information on these parameters for quadricyclane. In cases where the literature did not report the important parameters, we attempted to estimate the values by investigating parameters for comparable compounds or by giving ranges which can be expected for NAPLs. Finally, all the collected data was used to develop hypotheses concerning the behavior of quadricyclane in soils.

The first part of this review provides an overview of chemical properties of quadricyclane, as presented in the literature. The second section deals with thermodynamic and spectroscopic data of quadricyclane and norbornadiene. The third part of this review describes physical properties which are important for the fate and transport of quadricyclane in the subsurface. The review is concluded with a summary and conclusions section.

All data in this section are given in SI units, except for infrared frequencies which are commonly reported in cm^{-1} .

B. CHEMICAL PROPERTIES

Quadricyclane, (C_7H_8 , quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane) is commercially available from Aldrich Chemical Company. This thermally stable saturated hydrocarbon, is a relatively nonvolatile colorless liquid in its standard state (boiling point, 381 K at $9.9 \times 10^4 \text{ Pa}$; flash point, 284 K) (Aldrich Chemical Company, 1992; Domanski and Hearing, 1990; Gladysz et al., 1979).

Quadricyclane and substituted derivatives can be prepared by direct irradiation or by the photosensitized isomerization of norbornadiene or substituted derivatives of norbornadiene (Cristol and Snell, 1958; Hammond et al., 1961, 1964; Smith, 1973). This reaction and structures of norbornadiene and quadricyclane are shown in Figure 1.

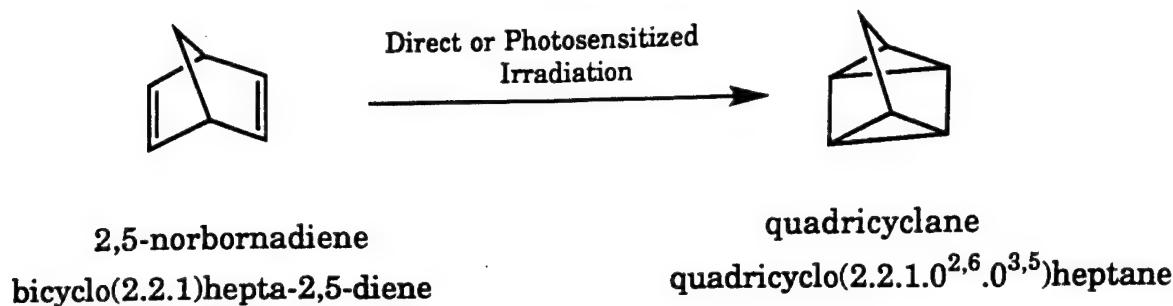


Figure 1. Synthesis of Quadricyclane from Norbornadiene.

The reverse isomerization has been observed when quadricyclanes are reacted with various transition metal complexes. Effective catalysts for the reverse isomerization are: η^4 -(norbornadiene) dichloropalladium (II) (Borsub and Katal, 1984), metal atoms (Gladysz et al., 1979) and rhodium catalysts (Cassar et al., 1970; Wiberg and Conn, 1976; Gassman et al., 1968; Hogeveen and Volger, 1967). Quadricyclane derivatives containing polar substituents (COOH, CONRR", COOCH₃) isomerize when heated in an aqueous alkaline solution containing a water soluble cobalt-phorphyrin complex (Co-TPPC) as shown in Figure 2 (Maruyama and Tamiaki, 1986). However, these workers found the quadricyclane derivatives to be thermally stable in aqueous sodium carbonate and to be unreactive to water at room temperature. To our knowledge, this is the only reported work where water was used as a solvent.

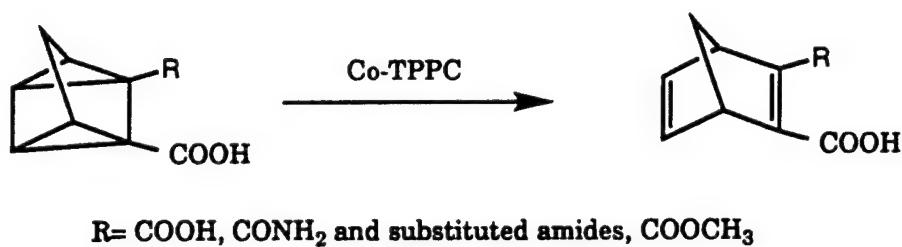


Figure 2. Catalyzed Isomerization of Substituted Quadricyclanes by a Cobalt Phorphyrin Complex in Aqueous Solution.

Schiff's base complexes of cobalt have also been shown to catalyze the conversion of quadricyclane into norbornadiene as shown in Figure 3 (Wöhrle et al., 1983).

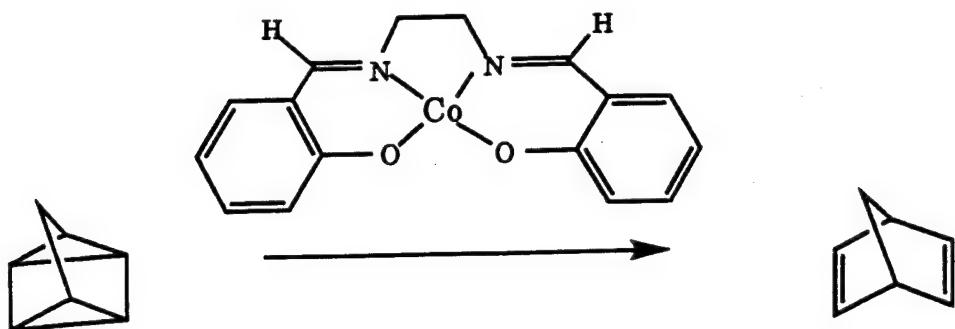


Figure 3. Isomerization of Quadricyclane to Norbornadiene by Schiff's Base Cobalt Complexes.

Fate of a cyclic hydrocarbon, like quadricyclane, in the aqueous environment must take into account the possibility of isomerization to the corresponding diene. Thus, the reactivities of quadricyclane and of norbornadiene must be considered.

Quadricyclane is highly strained and is thus reactive. It reacts with acetic acid to give a mixture of nortricyclyl acetate and exo-norbornyl acetate and it reacts with bromine to give 2,6-dibromonortricyclene and exo-5-anti-7-dibromonorbornene (Figure 4; Dauben and Cargill, 1961; Tabushi et al., 1976).

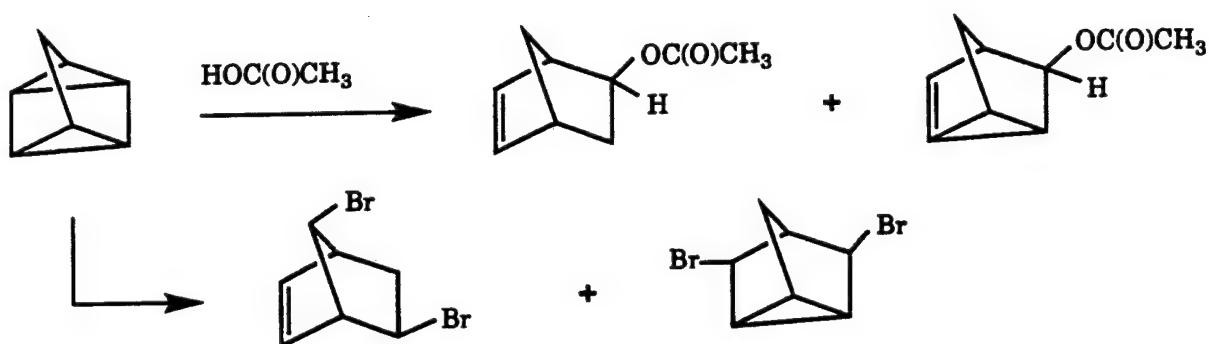


Figure 4. Reactions of Quadricyclane with Acetic Acid and with Bromine.

Reactions with electrophiles such as phosphonium ions (R_2P^+) will occur (Figure 5; Weissman and Baxter, 1987). The products shown in Figure 5 are due to the phosphonium ion bridging the 1,5 positions of the quadricyclane ring rather than the 2,3 positions.

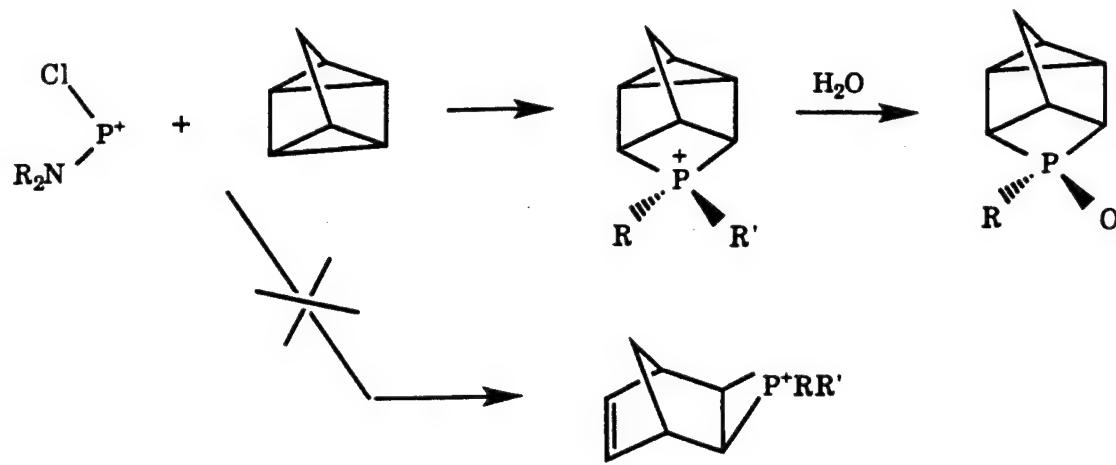


Figure 5. Reaction of Quadricyclane with Phosphonium Ions.

Electron transfer reactions can also occur as evidenced by the reaction of quadricyclane with Ag^+ (Figure 6; Koser and Faircloth, 1976).

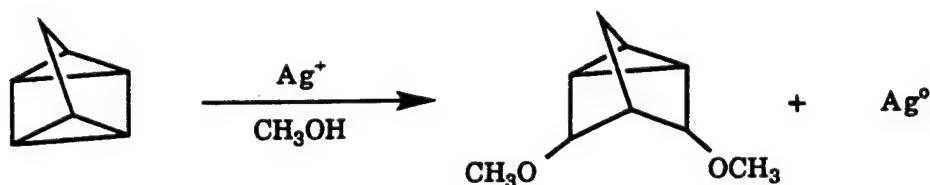


Figure 6. Oxidation of Quadricyclane by Silver(I).

The half-wave oxidation potential of quadricyclane in acetonitrile is 0.91 v versus a saturated calomel electrode (Gassman and Yamaguchi, 1982). This is a full volt lower than most other saturated hydrocarbons and the quadricyclane structure is more easily oxidized than norbornadiene which has a half-wave oxidation potential of 1.56 v.

Quadricyclane also undergoes cycloaddition reactions with a variety of dienophiles such as tetracyanoethylene to give 1:1 adducts (Figure 7; Smith, 1966).

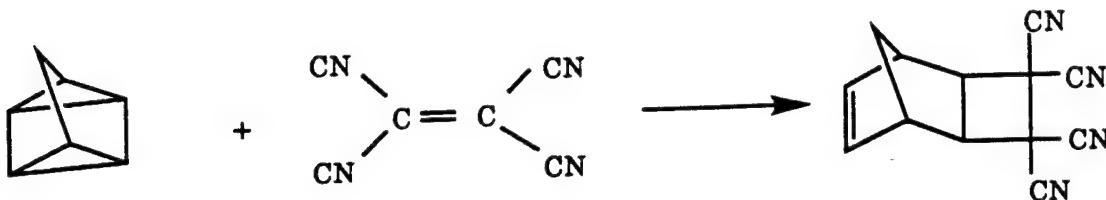


Figure 7. Reaction of Quadricyclane with Tetracyanoethylene.

Norbornadiene undergoes reactions typical of olefins. Thus electrophilic additions, such as the addition of acids or water in acid solution across the double bonds are likely, as are radical reactions, cycloadditions, oxidation at the double bond site, and the electrophilic addition of heavy metal compounds such as mercuric acetate.

The COD (Chemical Oxygen Demand) and the BOD (Biological Oxygen Demand) of norbornadiene have been determined in waste water obtained from a biological sanitary waste water treatment plant. The BOD analysis gave a value of 0.23 kg of oxygen /kg of norbornadiene and the COD was 2.36 kg oxygen/ kg of norbornadiene, suggesting low biodegradability over the five day period studied (Bridie et al., 1979).

C. SPECTROSCOPIC AND THERMODYNAMIC DATA

The first part of this section deals with spectroscopic properties of quadricyclane and norbornadiene molecules. These are important for analytical detection purposes. The remainder of the section provides an overview of thermodynamic properties of both compounds.

The ^1H nuclear magnetic resonance (NMR) spectrum of quadricyclane consists of resonances centered at 1.40 and 2.00 ppm, relative to tetramethylsilane, with an area ratio of 3:1. Thus the 1.4 ppm resonance is due to the protons attached to carbon 1-6 and the 2.00 ppm resonance is assigned to the protons attached to carbon 7. The infrared spectrum (carbon tetrachloride solution) consists of carbon-hydrogen stretching vibrations that appear as well resolved bands at 3069, 2929, and 2852 cm^{-1} (Smith, 1971; Dauben and Cargill, 1961).

The ^1H NMR spectrum of norbornadiene consists of resonances centered at 2.00, 3.50 and 6.75 ppm, relative to tetramethylsilane, with an area ratio of 1:1:2. The 2.00 ppm resonance is assigned to the protons on carbon 7, the 3.50 resonance to the protons on carbon 1 and 4 and the 6.75 resonance to the olefinic protons on carbon 2,3,5,6. The most important feature of the infrared spectrum is the cisoid olefinic CC stretch at 725 cm^{-1} (Pouchert, 1983; Dauben and Cargill, 1961).

A number of reports have been published on thermodynamic data for quadricyclane. A summary of the available data is presented here. Reported molar heat capacity data (at constant pressure) for

quadricyclane and norbornadiene are 139.13 J/(mol.K) for quadricyclane and 116.10 J/(mol.K) for norbornadiene (Hall et al., 1973). Other workers report molar heat capacities of 157.6 J/(mol.K) for quadricyclane and 161.2 J/(mol.K) for norbornadiene at 298.15 K (Domalski and Hearing, 1990).

The formation enthalpies based on calorimetric measurements of quadricyclane and norbornadiene are 325 ± 4 kJ/mol and 233 ± 4 kJ/mol, respectively (Kabakoff et al., 1975). The formation enthalpies as determined by combustion calorimetry are 253.3 ± 1.088 kJ/mol for quadricyclane and 211.7 ± 1.088 kJ/mol for norbornadiene (Hall et al., 1973).

We can calculate the reaction enthalpy of the isomerization of quadricyclane into norbornadiene by subtracting the formation enthalpy of norbornadiene from that of quadricyclane. The reaction enthalpies are -92 kJ/mol using the data of Kabakoff et al. (1975) and -42 kJ/mol using the measurements of Hall et al. (1973).

The vaporization enthalpies of quadricyclane and norbornadiene are 36.99 kJ/mol and 32.93 kJ/mol, respectively (Hall et al., 1973).

The isomerization of norbornadiene into quadricyclane has often been investigated as a possible way to store solar energy. The extra formation enthalpy of quadricyclane, as compared to norbornadiene, gives quadricyclane a very high enthalpy of combustion. The compound, therefore, has the potential to be an efficient fuel.

D. PHYSICAL PROPERTIES

This section considers physical properties of quadricyclane which are important in connection with its behavior in the subsurface environment. First, we discuss fluid properties of quadricyclane like density, viscosity, interfacial and surface tension, and molecular diffusion. Attention then shifts to partitioning processes in soils like sorption, dissolution and volatilization.

Quadricyclane is a nonpolar hydrocarbon and is therefore expected to be rather immiscible in water. It will therefore behave in the soil as a nonaqueous phase liquid (NAPL).

The density of quadricyclane in its liquid form is 919 kg/m^3 at $293 \pm 5 \text{ K}$ (specific gravity is 0.919) (Aldrich Chemical Company, 1992), which is lower than the density of water. Since the specific gravity of quadricyclane is less than unity, the liquid will behave as a light nonaqueous phase liquid (LNAPL). If a spill of a NAPL is large enough it will eventually reach the saturated zone in the subsurface. Here a LNAPL will start floating and spreading laterally above the capillary fringe (e.g., Mercer and Cohen, 1990).

The molecular weight of quadricyclane is 0.0921402 kg/mol (Domalski and Hearing, 1990). This means that the vapor of quadricyclane is denser than air and that gravity will force the vapor plume to sink in the vadose zone till it reaches the capillary fringe where it will spread laterally (e.g., Mercer and Cohen, 1990).

No data on the viscosity of quadricyclane could be found in the literature. The structure of the cyclohexane shows some similarity to that of quadricyclane and therefore we use the viscosity of this compound as a first estimate for the viscosity of quadricyclane. The viscosity of cyclohexane is $1.073 \times 10^{-3} \text{ kg/(m}\cdot\text{s)}$ and $0.899 \times 10^{-3} \text{ kg/(m}\cdot\text{s)}$ at 288 K and 293 K, respectively.

No data on the interfacial tension for quadricyclane could be found in the literature. However, interfacial tensions for NAPL-water generally range between 0.015 and 0.05 N/m (Mercer and Cohen, 1990).

The surface tension of cyclohexane is 2.382 and 0.2564 N/m at 288 and 293 K, respectively (Deisbach, 1963) (surface tension is defined as the interfacial tension at the interface between a substance and its own vapor).

Molecular diffusion coefficients for quadricyclane could not be found in the literature.

No data on aqueous solubility of quadricyclane could be found in the literature. Several methods have been proposed to estimate the solubility of organic compounds (Yalkowsky, 1992; Nirmalakhandan and Speece, 1988; Lyman et al., 1982). These methods, however, may not be very accurate for quadricyclane due to its rather complex structure. Cyclohexane, a compound rather similar in structure to quadricyclane, has a reported solubility of 56.1×10^{-3} kg/m³ at 293 K (Yaws et al., 1990). Cyclohexene, which may be compared with norbornadiene has an aqueous solubility at 293 K of 213×10^{-3} kg/m³ (Yaws et al., 1990). All immiscible liquids are at least slightly soluble in water. The solubility in water depends on temperature, cosolvents and salinity (ionic strength) (Mercer and Cohen, 1990). In the presence of humic substances like fulvic and humic acids, solubility limits can be two or three times the limits in pure water (Chiou, 1986, Senesi and Chen, 1989).

The presence of NAPLs in the subsurface may be a long term source of pollution as the NAPL slowly dissolves in water. Factors controlling NAPL dissolution into groundwater include the aqueous solubility, groundwater velocity, contact area between NAPL and water and the molecular diffusivity of the dissolved chemicals in water (Mercer and Cohen, 1990).

Because of the low solubility of most organic liquids, the impact of their dissolved molecules on the viscosity and density of the aqueous phase is generally negligible (Geller and Hunt, 1993). Since the dissolved NAPL is part of the aqueous phase, it can be transported by advection, diffusion and dispersion.

According to the manufacturer (Aldrich Chemical Company, 1992), the boiling point is 381 K (at 9.9×10^4 Pa). The vapor pressure of quadricyclane is 453 Pa at 302.7 K (Hall et al., 1973). The reported data indicate that quadricyclane is not very volatile. Gaseous phase vapors from NAPLs in the unsaturated zone can be the cause of further contamination of both groundwater and the soil (Huling and Weaver, 1992).

The behavior of quadricyclane in soils has, to our knowledge, never been investigated. Therefore, no information on partitioning coefficients related to sorption of quadricyclane in soils is available. Sorption refers to processes that remove molecules from the fluid phase and adheres them to the solid phase of the soil. In soils, a distinction has to be made between the organic matter and the soil minerals. Soil minerals are generally hydrophilic, which means that they are preferentially wetted by water. Organic matter, however, possesses hydrophilic in addition to hydrophobic sites (Mingelgrin and Prost, 1989). The uptake of nonionic organic chemicals by soils, containing water, is therefore controlled predominantly by the organic matter content (Chiou, 1989).

Although the partitioning of quadricyclane has not been investigated, much research has been done on the partitioning of other dissolved organic compounds between the aqueous and the solid

phase. So far, no general agreement has been reached on the sorptive mechanisms involved (Chiou, 1989). Numerous studies by Chiou (e.g. Chiou et al., 1979) show that the isotherms of non-ionic organic compounds in water are linear up to high relative concentrations (the ratio of equilibrium concentration to solute solubility). Furthermore, there appears to be no competition between two hydrophobic organic solutes in the uptake by soils, and the equilibrium heat for solute sorption is generally less exothermic than the inverse heat of solution into water (Chiou, 1989; Chiou et al., 1983). These observations lead to the postulation that removal of non-ionic organic compounds from the soil water consists mainly of solute dissolution into soil organic matter rather than physical adsorption. The inability of soil particles to adsorb organic solutes can be attributed to the strong dipole interaction of minerals with water (Goring, 1967), that excludes the organic compound from this portion of the soil. Mingelgrin and Gerstl (1983), however, point out that a Langmuir equation (which describes adsorption) also possesses a more or less linear ratio between the concentration of the solution and adsorbed species at low concentrations and they mention other experiments with hydrophobic chemicals which show a nonlinear isotherm. Senesi and Chen (1989) argue that the complexity of uptake processes on soil surfaces cannot simply be defined as an adsorption nor a partitioning process. They see it as a summation of the many possible mechanisms which are determined by the structural and chemical parameters of both adsorbed and sorbent.

A summary of the available physical property data on quadricyclane and norbornadiene is presented in Table 1. Important properties for which data are not available are also indicated in the table.

TABLE 1. SELECTED DATA ON QUADRICYCLANE AND NORBORNADIENE.

NAPL	quadricyclane	norbornadiene
Formula	C ₇ H ₈	C ₇ H ₈
Formula weight (kg/mol)	0.0921402	0.0921402
Specific gravity (-)	0.919	0.854
Viscosity [kg/ (m·s)]	n.a.	n.a.
Boiling point (K) (at 9.9 X 10 ⁴ Pa)	381	362
Interfacial tension between		
NAPL and water (N/m)	n.a.	n.a.
NAPL and air (N/m)	n.a.	n.a.
Aqueous solubility (mol/m ³)	n.a.	n.a.
Partitioning coefficients (-)	n.a.	n.a.

n.a. = not available

E. SUMMARY AND CONCLUSIONS

In this section, we present a summary of the main findings of this literature review, along with hypotheses about the expected behavior of quadricyclane in the subsurface.

The chemical and physical properties of quadricyclane have not yet been thoroughly investigated. Experimental data on its behavior in aqueous systems is very limited and no information on the fate of quadricyclane in the subsurface is available.

Quadricyclane is expected to behave as a LNAPL in the subsurface environment. The liquid is not very volatile under natural conditions.

Quadricyclane is very reactive due to its high strain energy. This makes it very likely that the chemical will undergo reactions in the subsurface environment.

Part of the NAPL will dissolve and become part of the aqueous phase. Aqueous- as well as nonaqueous-phase quadricyclane will tend to be sorbed into the organic matter.

Since the minerals, organic matter and the aqueous phase in soils contain a variety of metal complexes, quadricyclane may isomerize into norbornadiene. The type of cations in the soil and the stable form of these cationic species depend among others on soil type and pH.

Some compounds in the aqueous phase and the soil organic matter may act as electrophiles, which might react with quadricyclane to give water soluble derivatives.

Acids in soils may react with quadricyclane. Common acids in soils are, for example, humic and fulvic acids and inorganic acids like aquated Fe^{3+} and Al^{3+} .

Quadricyclane may undergo cycloaddition in soils since a variety of dienophiles can exist in especially the organic matter (e.g. Meikle, 1972). This may lead to new cyclic derivatives of quadricyclane.

The strongest oxidizing agents in soils are oxygen in aerobic conditions and nitrate in anaerobic soils (Bohn et al., 1983). These chemical species may oxidize quadricyclane.

Quadricyclane can be produced by exposing norbornadiene to sunlight. It is therefore unlikely that the compound will undergo photolytic transformations in the subsurface environment.

It should be noted that isomers, such as norbornadiene, and derivatives of quadricyclane, which are formed in soils, may react further to form new species.

When studying the behavior of highly strained hydrocarbons like quadricyclane in a soil environment, one should consider chemical reactions as a major factor. Each species obtained by these reactions has its own physical properties. This implies that in order to predict the fate of strained hydrocarbons in a specific soil, one should understand the chemical and physical behavior of the chemical and all its reaction products.

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SECTION III CHEMICAL ANALYSES OF QUADRICYCLANE AND ITS REACTION PRODUCTS

A. INTRODUCTION

This section describes the analytical procedures for the quantitative determination of quadricyclane and its reaction products in aqueous solution.

B. MATERIALS AND METHODS

Dodecane, norbornadiene, 5-norbornaden-2-ol, norcamphor, norborneol and quadricyclane were obtained from Aldrich Chemical Company and nortricyclyl bromide was obtained from Lancaster Synthesis, Inc. All were used without further purification. Quadricyclane and norbornadiene purity was determined by gas chromatography prior to each experiment.

1. Gas Chromatographic Analyses

Analyses were carried out on a Shimadzu GC14 gas chromatograph equipped with a flame ionization (FID) and an electron capture (ECD) detector, an AOC-17 autoinjector, and a CR501 computing integrator/data processor. The FID was coupled to a Restek RTX-1 capillary column (30 m, 0.25 mm ID) and the ECD was coupled to a Restek RTX-volatiles wide bore capillary column (30 m, 0.53 mm ID). All work reported here was analyzed by FID. To a weighed amount of the aqueous solution (typically 0.4-0.8 grams), 0.4-1.0 grams of a standard solution (881.8 ppm of decane in isopropanol) was added as an internal standard. In later experiments, an aqueous solution of isopropanol (96,579 ppm isopropanol) was weighed in as the internal standard. Multiple injections were made over the range of 0.2 to 1.0 μ L. Injections were made at 40°C. After holding for 4 minutes, the temperature was raised at a rate of 25°C/min to 200°C and held at that temperature for 10 minutes. The areas of the components of the solutions were plotted against the areas of the decane or isopropanol standard for each injection and the data fitted to a linear plot with correlation coefficients of greater than 0.99 (Figure 8).

2. Mass Spectral Analyses

Mass spectral analyses were carried out on a VG 7070 EHF mass spectrometer equipped with a Varian 3700 gas chromatograph and a data station. One micro liter aqueous injections were made at 40°C. After holding for 4 minutes, the temperature was raised at a rate of 25°C/min to 200°C and held at that temperature for 10 minutes. Ionization was carried out in the electron impact mode.

3. Solubility Studies of Quadricyclane and Norbornadiene

Early attempts at determining the solubility of quadricyclane in water revealed that quadricyclane has a great propensity to form micro emulsions in water. This is probably because it has a high density compared to other hydrocarbons (0.919 g/cm³), very near that of water itself. Several approaches were carried out to insure that microemulsions were not present.

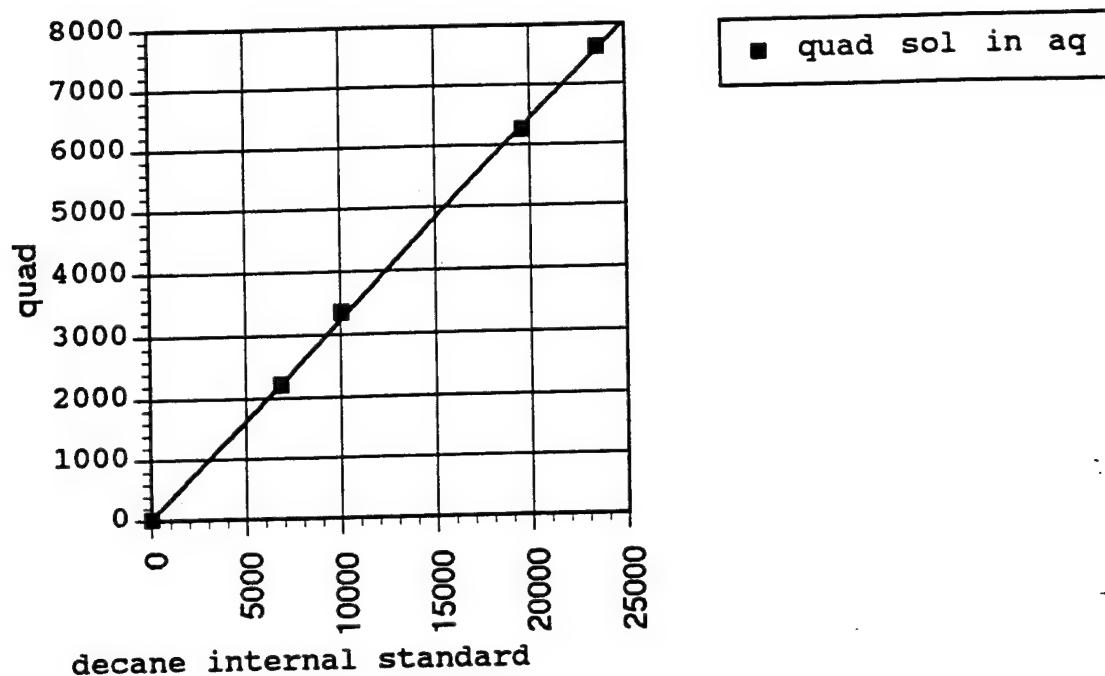


Figure 8. Typical Graph Obtained by the Multiple-Injection Method for Determining Quadricyclane Concentrations.

a. Centrifugation

One cm^3 of quadricyclane and 10 cm^3 of water were shaken mechanically for 15 min and then allowed to set undisturbed for 1 h. The top layer (excess quadricyclane) was removed by a pipette and the aqueous layer was transferred to a test tube, centrifuged for 15 min, and then injected into the gas chromatograph. The average quadricyclane concentration from three runs was 342 ppm.

b. Settling

One cm^3 of quadricyclane was added to 5 cm^3 of deionized water in a vial fitted with a cap and shaken by hand for 0.5 h. The cloudy emulsion was allowed to sit undisturbed for two days. A 1 cm^3 syringe with an 0.1 cm^3 of air was inserted to the bottom of the vial. The air was injected very slowly to minimize the disturbance and 1 cm^3 of the water layer was slowly withdrawn. The syringe needle was washed twice with deionized water and wiped dry. About 0.4 cm^3 of the sample was expelled. The aqueous layer was then analyzed by gas chromatography as described above. The result was 364 ppm solubility of quadricyclane.

In a variation of this procedure, a 5 cm^3 syringe was charged with 4 cm^3 of deionized water and 0.5 cm^3 of quadricyclane. The syringe was inverted and the air was expelled. A removable septum was then placed over the end of the syringe and the apparatus was vigorously shaken for 2 min and allowed to set undisturbed 0.5 h. To a weighed sample vial equipped with a syringe cap, decane-isopropanol standard was added and the aqueous quadricyclane solution was added displacing the air. Injections were made from this vial. The result was a solubility of 324 ppm for quadricyclane.

c. Filtration with 0.45 and $0.1 \mu\text{m}$ Microfilters

Aqueous solutions of quadricyclane obtained from (2) were filtered through 0.45 and $0.1 \mu\text{m}$ microfilters before gas chromatographic analysis. The results from these experiments were identical with those obtained in (b).

d. Column Elution

A glass column (350 mm long and 15 mm ID), equipped with a syringe needle as an outlet, was charged with 120 mm of dry sea sand obtained from Fisher Scientific Company. Quadricyclane, 0.6 cm^3 , was dripped onto the top of the sand taking care to spread it as evenly as possible. An additional 25 mm of sea sand was then added to the top of the column. The column was then left to stabilize for 1/2 h. Elution was then carried out with deionized water and samples were collected every 15 min. These samples were run immediately or kept on ice until tested. The results are reported in Figure 9. The maximum solubility was determined to be about 380 ppm.

Norbornadiene solubility was determined using the settling method described above in (b). A value of 260 ppm was obtained.

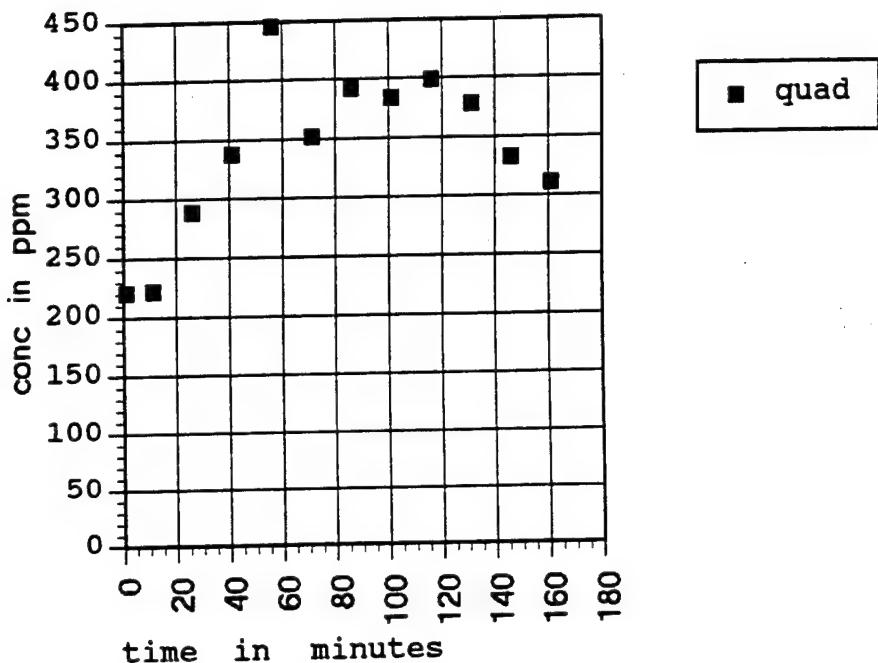


Figure 9. Quadricyclane Concentration as a Function of Time Obtained by Elution from a Column of Sea Sand.

4. Reaction of Quadricyclane and Water

To generate quantities of products of quadricyclane and water that would be great enough for identification, a reactor was set up containing deionized water with a quadricyclane layer on top of the water. After 9 days gas chromatographic analysis showed that the water layer had 42 ppm of quadricyclane, 215 ppm of the product with a retention time of 6.41 min and 3.815 ppm of the 6.79 min retention time product. A second apparatus containing D_2O and quadricyclane gave quite similar results with the products showing some deuterium incorporation into the parent ion. Mass spectral data are given in Tables 2, 3, 4, and 5.

TABLE 2. MASS SPECTRAL DATA OF WATER SOLUTIONS OF QUADRICYCLANE.¹

m/z	Relative Intensity ²				Assignment
	Quadricyclane	Norbornadiene	Product A	Product B	
39	24.1	14.0	17.7	51.4	C ₃ H ₃ ⁺
40				12.2	C ₃ H ₄ ⁺
41				38.2	C ₃ H ₅ ⁺
43				17.6	C ₃ H ₇ ⁺
51				14.4	C ₄ H ₃ ⁺
53				31.0	C ₄ H ₅ ⁺
54				25.1	C ₄ H ₆ ⁺
55				49.6	C ₄ H ₇ ⁺
65	36.8	14.0	15.6	18.1	C ₅ H ₅ ⁺
66	36.5	32.6	100.0	100.0	C ₅ H ₆ ⁺
67			20.4	78.3	C ₅ H ₇ ⁺
68				18.1	C ₅ H ₈ ⁺
69				22.2	C ₅ H ₉ ⁺
77				35.6	C ₆ H ₅ ⁺
78				17.8	C ₆ H ₆ ⁺
79			13.7	88.0	C ₆ H ₇ ⁺
80				11.9	C ₆ H ₈ ⁺
81				52.8	C ₆ H ₉ ⁺
82				18.9	C ₆ H ₁₀ ⁺
91	100.0	100.0		48.9	C ₇ H ₇ ⁺
92	42.0	47.9		29.3	C ₇ H ₈ ⁺
95				48.0	C ₆ H ₉ O ⁺
109				18.1	C ₇ H ₉ O ⁺
110			19.8	48.9	C ₇ H ₁₀ O ⁺

1. Quadricyclane and water aged for more than two weeks.

2. Intensities less than 10% were ignored.

TABLE 3. MASS SPECTRAL DATA FOR THE ENDO AND EXO FORMS OF
5-NORBORNEN-2-OL AND PRODUCTS OF QUADRICYCLANE
AND WATER.¹

m/z	Relative Intensity ²				Assignment
	exo/endo	endo/exo	Product A	Product B	
5-Norbornen-2-ol					
39	15.5	47.0	17.7	51.4	$C_3H_3^+$
40		22.8		12.2	$C_3H_4^+$
41		19.2		38.2	$C_3H_5^+$
43				17.6	$C_3H_7^+$
51		11.9		14.4	$C_4H_3^+$
53		13.1		31.0	$C_4H_5^+$
54				25.1	$C_4H_6^+$
55				49.6	$C_4H_7^+$
65	12.0	32.5	15.6	18.1	$C_5H_5^+$
66	100.0	100.0	100.0	100.0	$C_5H_6^+$
67	18.9	49.1	20.4	78.3	$C_5H_7^+$
68				18.1	$C_5H_8^+$
69				22.2	$C_5H_9^+$
77		17.2		35.6	$C_6H_5^+$
78				17.8	$C_6H_6^+$
79	12.4	24.5	13.7	88.0	$C_6H_7^+$
80				11.9	$C_6H_8^+$
81		12.4		52.8	$C_6H_9^+$
82				18.9	$C_6H_{10}^+$
91		10.0		48.9	$C_7H_7^+$
92				29.3	$C_7H_8^+$
95				48.0	$C_6H_7O^+$
109				18.1	$C_7H_9O^+$
110	17.7	41.0	19.8	48.9	$C_7H_{10}O^+$

1. Quadricyclane and water aged for more than two weeks.

2. Intensities less than 10% were ignored.

TABLE 4. MASS SPECTRAL DATA FOR PRODUCTS A AND B COMPARED TO NORCAMPHOR AND NORBORNEOL.

m/z	Relative Intensity ¹				Assignment
	Product A	Product B	Norcamphor	Norborneol	
39	17.7	51.4	41.0	30.1	C ₃ H ₅ ⁺
40		12.2			C ₃ H ₄ ⁺
41		38.2	36.1	40.0	C ₃ H ₅ ⁺
43		17.6		10.4	C ₃ H ₇ ⁺
51		14.4			C ₄ H ₅ ⁺
53		31.0	16.3	17.0	C ₄ H ₅ ⁺
54		25.1	37.1		C ₄ H ₆ ⁺
55		49.6	11.0	23.1	C ₄ H ₇ ⁺
56				12.9	C ₄ H ₈ ⁺
57				34.0	C ₄ H ₉ ⁺
65	15.6	18.1			C ₅ H ₅ ⁺
66	100.0	100.0	89.8	76.8	C ₅ H ₆ ⁺
67	20.4	78.3	100.0	89.5	C ₅ H ₇ ⁺
68		18.1	18.3	81.8	C ₅ H ₈ ⁺
69		22.2			C ₅ H ₉ ⁺
70				15.9	C ₅ H ₁₀ ⁺
77		35.6			C ₆ H ₅ ⁺
78		17.8			C ₆ H ₆ ⁺
79	13.7	88.0		91.9	C ₆ H ₇ ⁺
80		11.9			C ₆ H ₈ ⁺
81		52.8	20.6	14.7	C ₆ H ₉ ⁺
82		18.9			C ₆ H ₁₀ ⁺
83				19.1	C ₆ H ₇ ⁺
91		48.9			C ₇ H ₇ ⁺
92		29.3			C ₇ H ₈ ⁺
94				100.0	C ₇ H ₁₀ ⁺
95		48.0			C ₆ H ₇ O ⁺
109		18.1			C ₇ H ₉ O ⁺
110	19.8	48.9	47.4		C ₇ H ₁₀ O ⁺

1. Intensities less than 10% were ignored.

TABLE 5. MASS SPECTRA OF PRODUCT B IN THE REACTION OF QUADRICYCLANE WITH WATER COMPARED TO PRODUCTS OBTAINED FOR THE REACTION OF WATER WITH OTHER CYCLIC COMPOUNDS.

m/z	Product B	Relative Intensity ¹		
		Nortricyclyl bromide in water	Norbornadiene in water with HBr ²	Quadricyclane in water with HBr
39	51.4	48.2	44.0	32.6
40	12.2			
41	38.2	37.1	32.3	19.9
43	17.6	12.1	14.8	10.5
50		12.2		
51	14.4	22.4	10.8	15.5
53	31.0	34.2	28.1	26.7
54	25.1	26.0	23.1	19.4
55	49.6	51.2	44.2	51.4
65	18.1	30.1	21.1	26.1
66	100.0	95.0	100.0	91.0
67	78.3	82.8	74.5	80.8
68	18.1	24.2	13.5	25.4
69	22.2	19.2	23.1	24.1
77	35.6	53.2	35.7	51.5
78	17.8	16.7	19.2	22.0
79	88.0	100.0	85.0	100.0
80	11.9		10.1	14.0
81	52.8	73.3	56.5	69.0
82	18.9	19.5	13.8	26.6
91	48.9	66.2	46.6	77.3
92	29.3	24.8	30.6	29.1
95	48.0	50.0	43.9	62.4
109	18.1		22.6	24.6
110	48.9	27.3	51.1	31.3

1. Intensities less than 10% relative abundance are not listed.

2. This is one of several products.

C. ANALYTICAL PROCEDURES FOR QUADRICYCLANE EXTRACTED FROM SOILS

The extraction procedure and results are reported in Section V. Dodecane extracts were weighed and the amount of quadricyclane in the extract was determined by taking 0.4 to 0.5 grams of the extract, adding 0.275 grams of standard (decane @ 4,981 ppm in dodecane) to the first extract or 0.05 grams of standard to the second extract, and injecting into the gas chromatograph. Multiple injections were made over the range of 0.4-1.0 μ L. The column temperature was 40°C upon injection. After holding for 4 minutes, the temperature was raised at a rate of 25°C/minute to 200°C and held at that temperature for 10 minutes.

D. RESULTS AND DISCUSSION

The aqueous solubility of quadricyclane from the approaches described above gave an average of 352 ppm. The solubility of norbornadiene was found to be 260 ppm.

During the solubility measurements of quadricyclane, it was noted that the concentration of quadricyclane in water diminished with time. Thus, an aqueous solution containing 107 ppm of quadricyclane showed a decrease to 25 ppm in 24 hours and no quadricyclane could be detected after 4 days. This disappearance was coupled with the appearance of two new peaks in the gas chromatogram with retention times of 6.41 and 6.79 min. The mass spectra of the products are given in Table 2 along with the mass spectra of quadricyclane and norbornadiene. Assignments were made and the fragmentation pattern of quadricyclane is given in Figure 10 and that of 5-norbornen-2-ol in Figure 11. A comparison of the fragmentation pattern of 5-norbornen-2-ol with that of product A observed at 6.41 minutes in the gas chromatogram of the products given in Table 3-2 leaves little doubt as to its identity. Furthermore, although 5-norbornen-2-ol exists in endo and exo isomers, only one of the isomers is formed (Table 3). At present, assignment of the product to the exo or endo form is not possible although one can rationalize that the exo isomer should be preferred.

A far more complicated fragmentation pattern is observed for product B (Table 4). In order to identify product B, mass spectra of several possible candidates were obtained and these are reported in Table 4 and 5. Examination of the data reported in Table 4 for norcamphor and norborneol reveals that neither of these correspond to product B. A comparison of the mass spectrum of product B with that of nortricyclyl bromide in water is given in Table 5. Of interest is the fact that no bromide containing species is observed for the nortricyclyl bromide in water suggesting that the Br is quite labile and that a species identical to product B is formed. We have tentatively assigned both products to be nortricyclyl alcohol based on the highest mass ion at m/z 110 and the fact that both fragmentation patterns are so similar. Table 5 also reveals that both norbornadiene and quadricyclane form nortricyclyl alcohol.

A possible reaction scheme for the reaction of quadricyclane in water is shown in Figure 12. This reaction scheme involves electrophilic attack of H^+ on one of the carbons in a three-membered ring to give a carbonium ion which may add OH^- to give nortricyclyl alcohol or may rearrange first and then add OH^- to give 5-norbornen-2-ol.

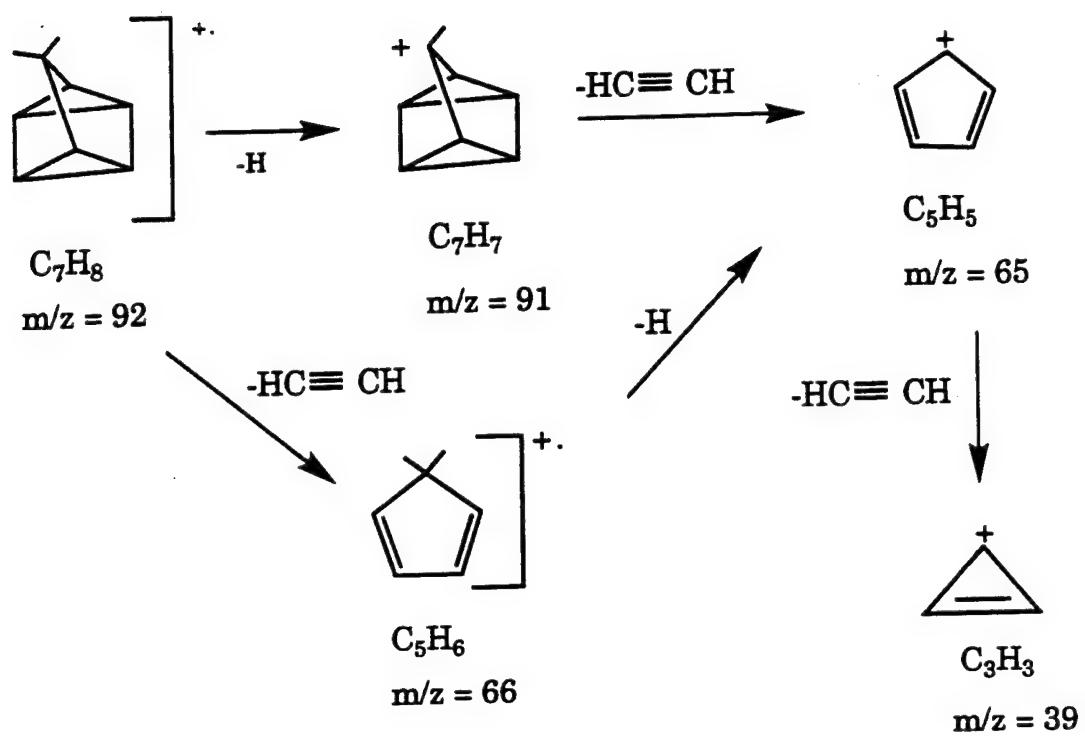


Figure 10. Mass Fragmentation Pattern for Quadricyclane.

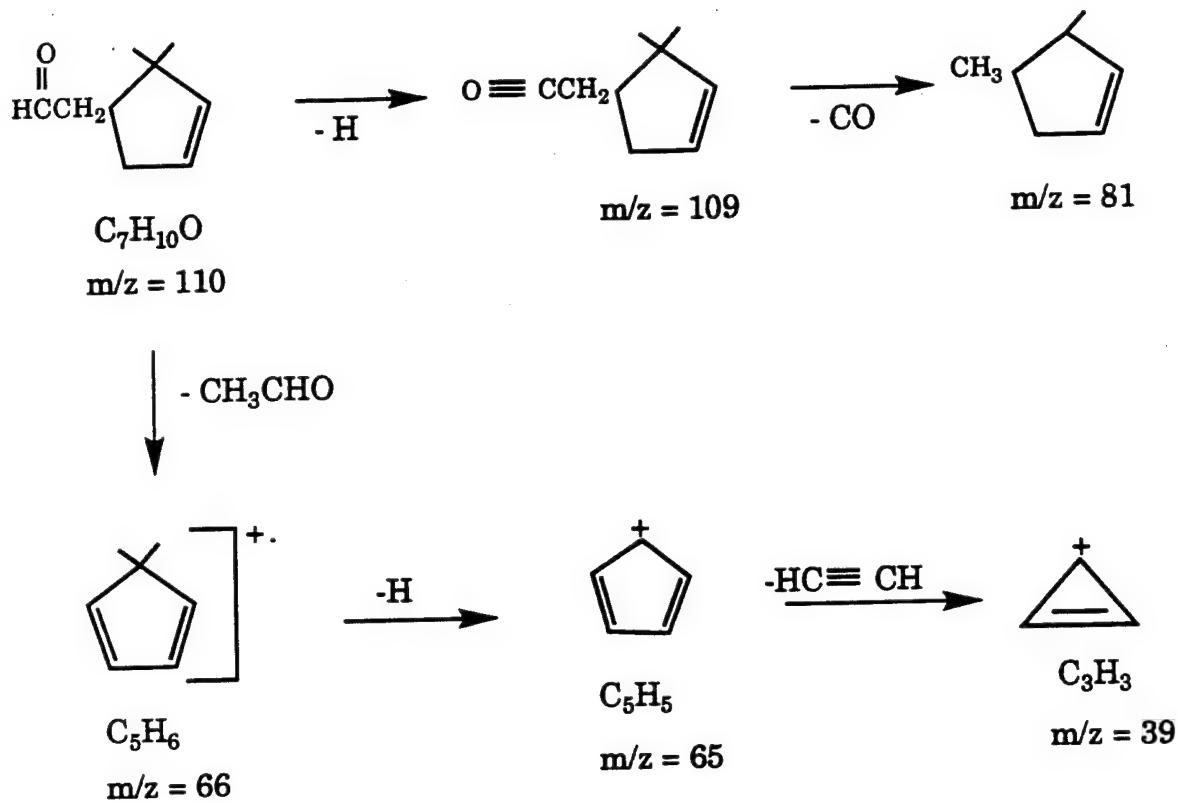


Figure 11. Mass Fragmentation Pattern for 5-Norbornen-2-ol.

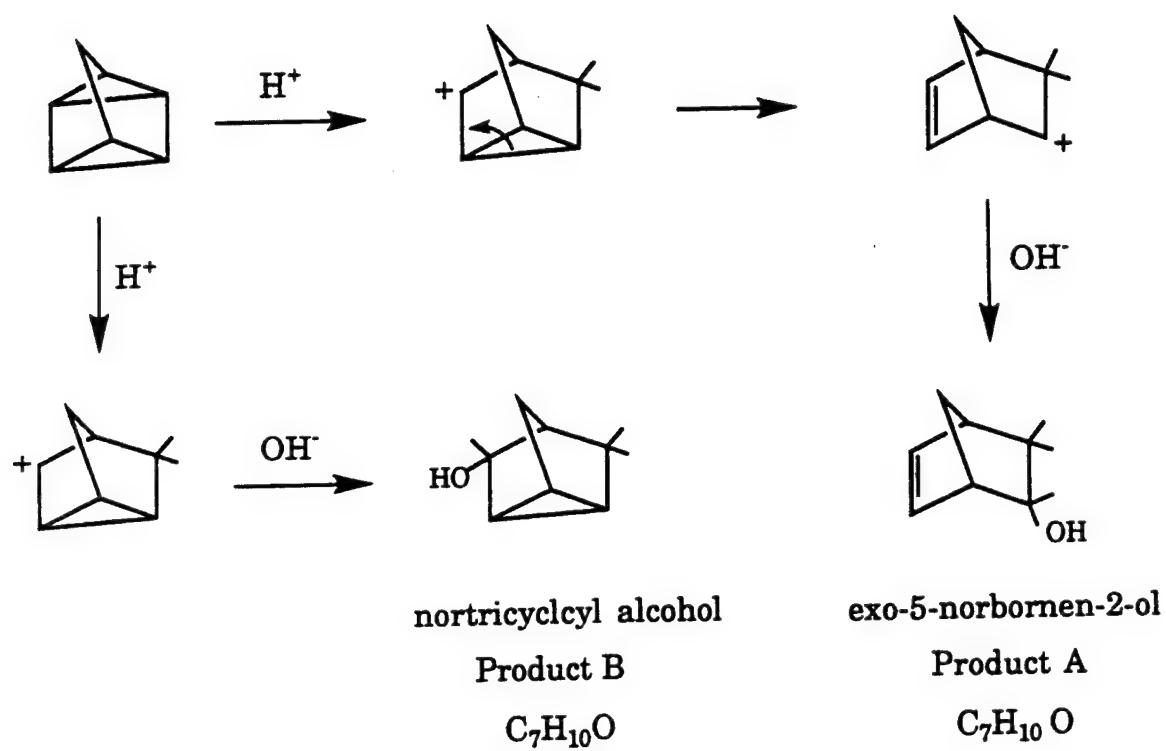


Figure 12. Reaction Scheme for the Reaction of Quadricyclane with Water.

SECTION IV COLLECTION AND ANALYSIS OF TEST SOILS

A. INTRODUCTION

One of the main objectives of the current research project is an investigation into the fate of quadricyclane in different natural soil environments. Therefore, two soils with a rather high pH and two soils with a relatively low pH were collected. Within each of these two categories, we collected a soil which naturally occurs with a low and one with a high organic matter content. An additional goal was to select soils with similar but rather small, clay fractions. Only topsoil (first 20 cm of homogeneous A horizon) was collected.

Two soils types with a relatively low pH were collected in Geneva county, Alabama, near the Florida border. The two high pH soils were obtained from Sevier County near Knoxville, Tennessee.

B. ANALYSIS

Upon collection, the soils were air-dried and passed through a 2-mm sieve before further analyses and subsequent experiments.

Unless otherwise indicated the reader is referred to the Soil Survey Laboratory Methods Manual (National Soil Survey Center, 1991), which describes each analysis in detail.

1. Classification

Soil classification information is given in Table 6.

TABLE 6. CLASSIFICATION OF SOILS AND ACRONYMS ASSIGNED TO EACH SOIL TYPE.

Soil acronym*	Family description	Order
ALOHPL	Typic Kanhaplauults	Ultisol
ALOLPL	Plintic Kandiudults	Ultisol
TNOHPH	Cumulic Hapduudolls	Mollisol
TNOLPH	Typic Eutrochrepts	Inceptisol

* The first part of the acronyms (AL or TN) indicate the State of origin of the soil; OL and OH indicate a low and high organic matter content, respectively, and PL and PH refer to the low and high pH soil, respectively.

2. pH and Organic Matter Content

A dual electrode pH meter was used to measure the pH of suspensions consisting of 20 grams of soil material and 20 ml of water (Table 7).

Organic matter contents (Table 7) were determined by a dry combustion method. The amounts of carbon, measured with a LECO WR-12 carbon analyzer, were multiplied by a factor 1.9 to account for elements other than C, which are part of the organic matter.

TABLE 7. pH VALUES OF SUSPENSIONS CONSISTING OF 20 cm³ OF WATER IN EQUILIBRIUM WITH 20 GRAMS OF SOIL, AND % ORGANIC MATTER CONTENT FOR FOUR DIFFERENT SOIL TYPES.

Soil acronym	pH	% organic matter
ALOHPL	4.60	6.0
ALOLPL	5.12	1.0
TNOLPH	5.93	2.2
TNOHPH	6.35	2.8

3. Particle Size Analysis

The particle size distributions were determined by the pipette method, which allowed the soil particles for each soil to be divided into three size groups: sand, silt and clay (Table 8). The size fractions were used to determine the soil texture for each soil (Table 8) according to the USDA classification scheme (Gee and Bauder, 1986). The % clay is very similar for all four soils.

TABLE 8. PARTICLE SIZE DISTRIBUTION (WEIGHT BASIS) FOR FOUR DIFFERENT SOIL TYPES.

Soil acronym	% Sand	% Silt	% Clay	soil texture
ALOHPL	70.2	18.4	11.4	sandy loam
ALOLPL	77.8	11.0	11.2	sandy loam
TNOLPH	57.5	30.2	12.3	sandy loam
TNOHPH	48.0	37.6	14.4	loam

4. Mineralogical Composition

The mineralogical composition of the clay fractions (Table 9) was analyzed by X-ray diffraction in conjunction with thermal gravimetric analysis. The X-ray analysis was performed with a Siemens D5000 X-ray spectrometer and the gravimetric analysis with a Du Pont 951 thermogravimetric analyzer (Karathanasis and Hajek, 1984).

TABLE 9. MINERALOGICAL COMPOSITION FOR FOUR SOIL TYPES.

Soil acronym	Mineralogical composition*
ALOHPL	interlayered vermiculite (5), kaolinite (4), gibbsite (2), quartz (2), goethite (1)
ALOLPL	goethite (trace), quartz (1), kaolinite (4), interlayered vermiculite (5)
TNOLPH	quartz (1), mica/interstratified vermiculite (1), kaolinite (2), illite (4), vermiculite (3)
TNOHPH	mica/interstratified vermiculite (1), quartz (1), kaolinite (2), vermiculite (4), illite (4)

* The numbers between brackets denote a semi quantitative rank based on interpretation of the X-ray diffraction pattern (Hajek, 1994, personal communication): (5) is dominant (> about 50%), (4) is about 30 to 40%, (3) is about 20 to 30%, (2) is about 10 to 20%, and (1) is less than 10% of the clay fraction.

5. Exchangeable Cations

Exchangeable cations are cations which can be extracted from the soil by salt solutions. Concentrations of exchangeable Mg^{2+} , Ca^{2+} , K^+ and Na^+ were determined by shaking 5 grams of soil with a 1 M NH_4OAC solution (Table 10). The abundant NH_4^+ cations displace most of these cations at the available adsorption sites. The exchangeable Al (Table 10) was determined by shaking the samples with a 1 M KCl solution. A mechanical vacuum extractor was used to extract the salt solutions from the suspensions for analysis by an atomic adsorption spectrophotometer (Instrumental Laboratory, Model 251).

TABLE 10. EXCHANGEABLE CATIONS FOR FOUR SOIL TYPES IN CENTIMOLES PER KG OF SOIL.

Soil acronym	Exchangeable cations				
	Ca^{2+}	Mg^{2+}	K^+	Al^{3+}	Na^+
----- cmol/kg -----					
ALOHPL	0.34	0.13	0.05	3.50	0.12
ALOLPL	0.30	0.16	0.08	0.39	0.13
TNOLPH	2.92	0.83	0.07	0.06	0.12
TNOHPH	4.63	1.52	0.08	0.09	0.12

6. Cation-Exchange Capacity

The cation-exchange capacity (CEC) is defined as the capacity of a soil to sorb or hold cations and to exchange species of these ions in reversible chemical reactions (Buol et al., 1980).

The CEC was determined by two different methods. The CEC values at neutral pH (CEC-7, Table 11) were determined by first washing the samples with a normal NH_4OAC solution. Subsequently the NH_4^+ saturated soils were rinsed twice with ethanol to remove the nonadsorbed NH_4^+ . The samples were then leached with a normal KCl solution to displace the sorbed NH_4^+ . The amounts of ammonia in the leachate solutions were determined using Kjeldahl distillation and titration. CEC values were also determined using the method described by Hajek et al. (1972). In their approach, the exchangeable acidity (mostly Al) is estimated by the pH change of a buffered solution - soil suspension (Adams and Evans, 1962). The exchangeable bases were determined by shaking 4 cm^3 of soil in 20 mL of 0.05 N HCl + 0.025 N H_2SO_4 solution for 5 minutes, filtering the suspension, and analyzing the filtrate for exchangeable bases. The CEC at the natural pH of the soil (CECE, Table 11) was then calculated as the sum of the exchangeable bases and acidity. Besides the CEC of the soils, the CEC values of the clay fractions only were measured.

The CEC-7 is clearly higher than the CECE for all cases. The ratio between the CEC-7 and the CECE is larger for the low pH soils. This can, at least partly, be explained by the lower pH at which the CECE is determined. The excess negative charge, which is developed at high pHs in soils is known as pH dependent-charge (Bohn et al., 1985).

TABLE 11. CATION EXCHANGE CAPACITY IN CENTIMOLES OF CHARGE PER kg OF SOIL FOR FOUR SOIL TYPES AND THEIR CLAY FRACTIONS FOR A NEUTRAL pH (CEC-7) AND FOR THE NATURALLY OCCURRING pH (CECE).

Soil acronym	CEC-7	CECE	CEC-7	CECE
	(cmol _c .kg ⁻¹)			
	soil		clay fraction	
ALOHPL	10.61	4.14	93.43	36.41
ALOLPL	2.21	1.06	19.43	9.49
TNOLPH	6.92	4.00	56.15	32.45
TNOHPH	9.92	6.44	68.69	56.15

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SECTION V BATCH EXPERIMENTS WITH QUADRICYCLANE AND TEST SOILS

A. INTRODUCTION

The formation enthalpy of quadricyclane has been reported to be 325 kJ/mol (Kabakoff et al., 1975) and 253.3 kJ/mol (Hall et al., 1973). These rather high formation enthalpies causes the compound to be very reactive. Reported reactions involving quadricyclane include the catalyzed isomerization into 2,5-norbornadiene, the reaction with acetic acid and electrophiles, cycloaddition reactions with several dienophiles and electron transfer reactions (Section II).

Natural soils generally contain a wide variety of chemical species. This implies that one or more of the reactions described above may occur in the soil environment. Furthermore, the reaction products of these reactions may undergo further reactions. The formation enthalpy of quadricyclane is so high that it may take several reactions before the compound is in chemical equilibrium in the soil environment. The kind and number of reactions may be soil dependent. This section describes an experiment, which has been conducted in the past year to investigate the chemical behavior of quadricyclane in four selected soils. Some preliminary results will be presented.

B. MATERIALS AND METHODS

Quadricyclane was obtained from Aldrich Chemical Company. Before each experiment the purity of the liquid was measured by gas chromatography (GC). The soil types used are described in Section IV.

Ten grams of each soil was placed in a vial and 2 mL of deionized water and 3 mL of quadricyclane was added. Most of the liquid infiltrated into the soil samples. We used 12 instead of 10 grams of the ALOLPL soil, because the porosity of this soil appeared to be somewhat lower. The vials were gently rotated for various periods of time in a jarmill.

The extraction procedure consisted of three steps (Figure 13). First, the samples were removed from the vials and placed in 250 mL centrifuge bottles. Subsequently, 75 mL of dodecane (Aldrich Chemical Company) and 30 mL of a saturated NaCl solution was added. Dodecane was chosen as the solvent because of its favorable retention time on the GC, its low specific gravity of 0.749 (Aldrich Chemical Company, 1992), and its low volatilization, which made unsupervised shaking possible. The saturated NaCl solution was used because of its relatively high density, which minimizes the formation of micelles in the aqueous phase. Furthermore, the high ionic strength decreases the solubility of hydrocarbons. Preliminary experiments also indicated that quadricyclane is chemically stable in a NaCl solution, at least for short periods of time.

The centrifuge bottles were shaken for about 12 hours with a mechanical shaker. Subsequently, the bottles were centrifuged to separate the soil, aqueous extractant and the dodecane extractant. The two liquids were decanted from the centrifuge bottle into a separation funnel and the two immiscible liquids were separated. The extraction with dodecane and NaCl solution was conducted twice. Dodecane extractants were analyzed as indicated in Section III.

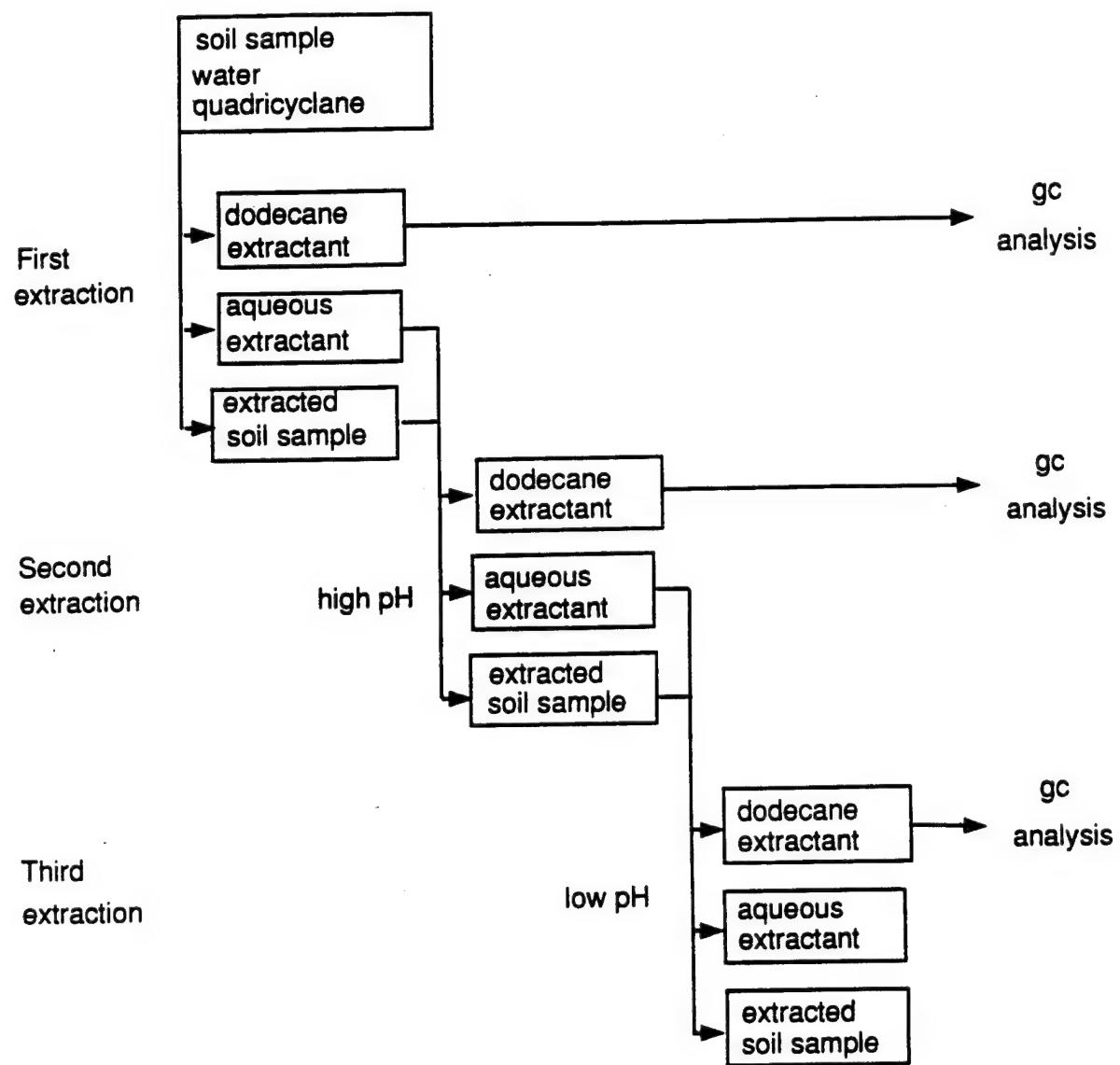


Figure 13. Extraction Procedure for Quadricyclane and Its Reaction Products from the Soil Samples.

The aqueous extractant could not be analyzed directly, because it clogs up the GC column, and was therefore subjected to a pH swing. This treatment was an attempt to make any water miscible reaction products of quadricyclane present in the aqueous solution to become water immiscible. The extracted soil material was also included in the pH swing. To obtain a high pH suspension, 100 mL of a NaOH solution at pH 14 was added to the soil samples. The mixture was then shaken manually for a few minutes and vacuum filtrated. Subsequently, 100 mL of aqueous extraction was added to the filtrate and the pH was checked with a universal pH meter to ensure a pH value of at least 12. Next, 50 mL of dodecane was added and the entire mixture was poured into a separation funnel. The drop funnel was shaken for several minutes before the two liquids were separated. The dodecane extractant was analyzed on the GC as described above. To obtain a low pH mixture, 100 mL of a HCl solution at pH 0 was added to the filtrated soil material and again the mixture was shaken for several minutes. The mixture was then vacuum filtered and the separated aqueous solution from the previous step was added to the filtrate. Again the pH was checked and the HCl solution was added when this pH was higher than 2. The extraction procedure with the dodecane was repeated.

The performance of the extraction was measured by comparing the total mass of the extracted quadricyclane and its reaction products with the mass of the quadricyclane which was initially added to the soil samples. The effect of the extraction procedure on the final analytical results was determined by extracting soil samples immediately after the water and the quadricyclane had been added.

C. RESULTS

The preliminary results of the chemical analysis of the dodecane extractant are shown in Table 12. The data of the immediate extraction (time = 0) indicate that the procedure of shaking and centrifuging with NaCl solution and dodecane does not have a significant effect on the reactions of quadricyclane. Only the extractant of the ALOHPL showed a trace of two reaction products. Furthermore, the ratio between the quadricyclane and the norbornadiene was close to that of the added mixture for all four soils.

Overall it appears that the pH of the soil is by far the most important factor for chemical stability of quadricyclane. After 98 days, at least half of the original amount of the quadricyclane in the ALOHPL soil was transformed. One of the reaction products has been identified as 5-norbornen-2-ol (Section III). The other product is yet to be identified. Both products appear to have a rather high solubility in water (Section III), and it is therefore likely that the NaCl extractant (which is yet to be analyzed) contains significant amounts of these species. The rate of the cycloadditions reactions clearly depends on the concentration of H^+ . The depletion of quadricyclane by isomerization into norbornadiene appears to be of less importance in the more acidic soils, but could be more important in soils with a near neutral pH. Further experiments with longer exposure time are needed to determine the significance of this reaction.

TABLE 12. RESULTS OF THE CHEMICAL ANALYSIS OF THE DODECANE EXTRACTANT FROM THE EXTRACTION OF FOUR SOIL SAMPLES INITIALLY CONTAINING 3 mL OF QUADRICYCLANE AND 2 mL OF WATER, WITH 30 mL OF NaCl SOLUTION AND 70 mL OF DODECANE, AFTER 0, 14, AND 98 DAYS.

Time, t, and Soil acronym	quadricyclane	2,5-norbornadiene	5-norbornen-2-ol	unknown product	recovery efficiency
-----grams-----					
%					
$t = 0$ days					
ALOHPL	1.83	0.05	d *	d *	68
ALOLPL	2.12	0.05	0.00	0.00	78
TNOLPH	2.24	0.06	0.00	0.00	83
TNOHPH	2.18	0.06	0.00	0.00	81
$t = 14$ days					
ALOHPL	1.95	0.07	0.09	0.08	79
ALOLPL	2.37	0.07	0.03	0.04	90
TNOLPH	2.77	0.09	0.01	0.01	104
TNOHPH	2.81	0.09	0.00	0.01	105
$t = 98$ days					
ALOHPL	1.10	0.12	0.43	0.39	73
ALOLPL	2.15	0.09	0.19	0.28	97
TNOLPH	2.65	0.12	0.03	0.03	103
TNOHPH	-	-	-	-	-

*d indicates a trace which was detectable but not measurable.

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SECTION VI
ONE-DIMENSIONAL (1-D) COLUMN EXPERIMENTS
WITH TETRACHLOROETHYLENE (PCE)

A. INTRODUCTION

An essential component in understanding and simulating multiphase fluid flow is the accurate determination of the hydraulic properties of the different fluids involved. One constitutive relationship, often used in computer codes, is the relation between the capillary pressure (P_c) and saturation (S) or volumetric fluid content (θ).

This section describes the measurement of the retention curves in a PCE-air and a water-PCE system.

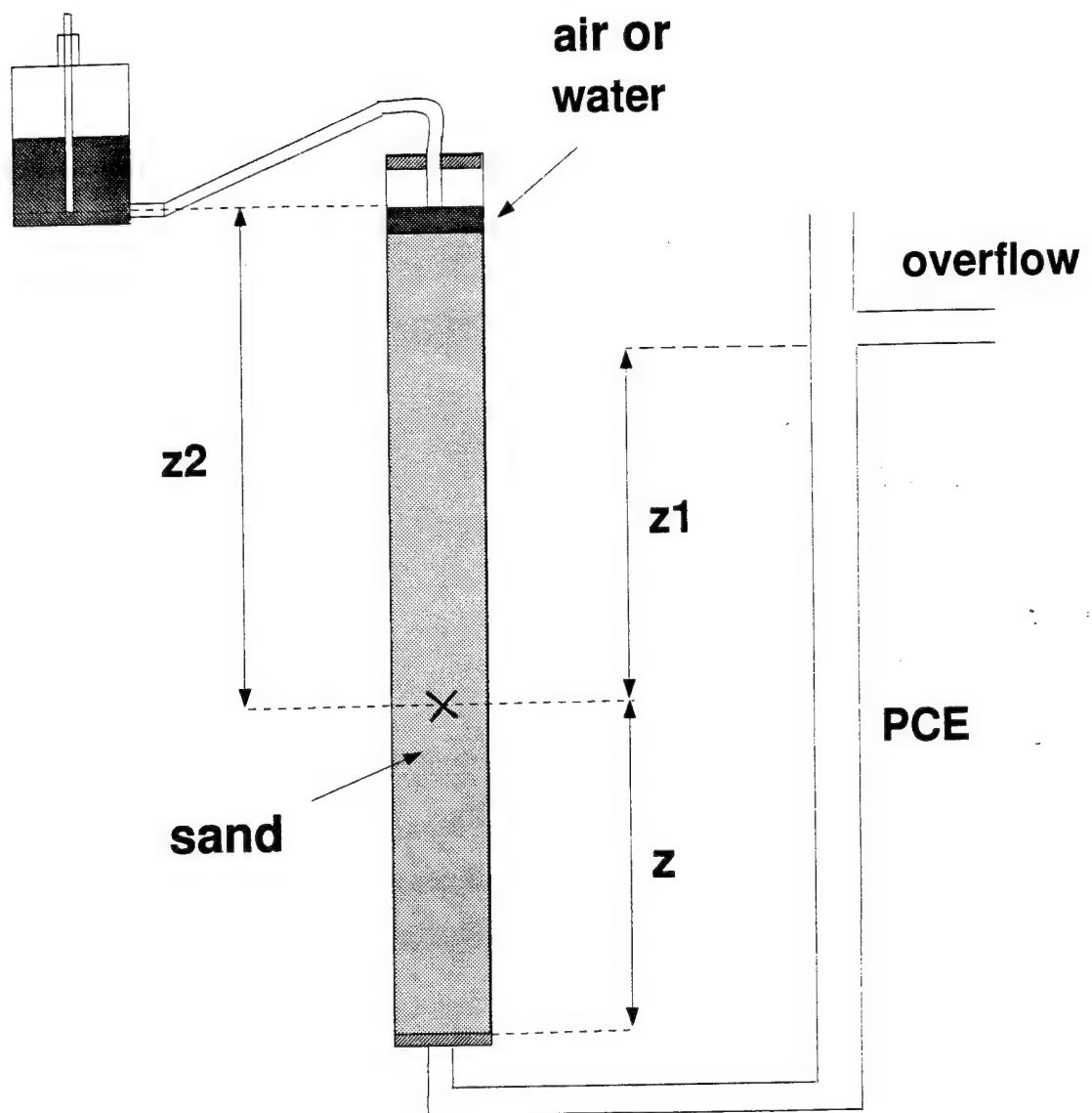
B. MATERIALS AND METHODS

A long-column experiment, as designed by Dane et al. (1992), was used to determine $P_c(S)$ relations. A 1-m long glass column (I.D. = 8.0 cm) with teflon end caps, was packed as uniformly as possible with clean oven-dry Flintshot 2.8 Ottawa sand (US Silica, Ottawa, Illinois), following the procedure of Dane et al. (1992). The height of the sand was 0.95 m. The outlet at the bottom of the column was connected to a reservoir of PCE (Tetrachloroethylene or Tetrachloroethythene 99%. Aldrich Chemical Company Inc, Milwaukee, Wisconsin), indicated as an overflow in Figure 14, which was raised or lowered to adjust the fluid pressures in the column.

For the PCE-air system, the initially oven-dry column was subjected to the following steps:

- 1 - Imbibition of PCE from the bottom of the column by slowly raising the reservoir until the PCE was ponded on top of the sand.
- 2 - PCE displaced by air by stepwise lowering the reservoir until the change in PCE content became negligible at all locations where the retention curves were determined.
- 3 - Air displaced by PCE by stepwise raising the reservoir until the PCE was ponded on top of the soil.
- 4 - Stepwise lowering and raising the reservoir to determine a scanning path.

After each change in elevation, the system was allowed to come to mechanical equilibrium. To assure that no more flow occurred, flow rates were occasionally checked with a buret, installed between the column and the reservoir of PCE, by closing a stopcock valve located between the buret and the reservoir. The small cross sectional area of the buret allowed to detect small fluxes of PCE. Upon reaching mechanical equilibrium during Steps 2 through 4, volumetric fluid contents were determined at specific locations (Table 13) along the length of the column with a dual-energy gamma radiation system (Ferrand et al., 1986; Ferrand et al., 1989; Oostrom and Dane, 1990). The diameter of the photon beam of this instrument is 6 mm.



X - Point of Measurement

Figure 14. Simplified Schematic of the Experimental Setup.

TABLE 13. VALUES FOR THE BULK DENSITY OF FLINTSHOT 2.8 OTTAWA SAND (ρ_b), THE CORRESPONDING POROSITY (ϵ) BASED ON A PARTICLE DENSITY OF 2.65 g cm^{-3} , AND THE AVERAGE VOLUMETRIC PCE CONTENT (θ_{pce}) DURING PCE SATURATED CONDITIONS.

Location	z^* (cm)	ρ_b (g cm^{-3})	ϵ (-)	θ_{pce} (-)
6	87.5	1.693	0.361	0.301
7	86.5	1.679	0.366	0.297
8	85.5	1.675	0.368	0.304
9	84.5	1.666	0.371	0.304
10	83.5	1.662	0.373	0.305
11	82.5	1.640	0.381	0.311
12	77.5	1.632	0.384	0.317

* z is the elevation of the measurement location relative to the bottom of the 1-m long column (Figure 14).

The capillary pressure head (h_c) is defined as the difference between the pressure head of the nonwetting fluid (h_{nw}) and the wetting fluid (h_w). In a PCE-air system, PCE is the wetting fluid and air the nonwetting fluid. The resistance to air flow is assumed to be negligible, so that the pressure head of the nonwetting fluid is zero throughout the continuous gaseous phase. The equation for the capillary pressure head for the PCE-air system reads:

$$h_c = -h_w = \frac{-P_w}{\rho_{h_2o} \cdot g} \quad (1)$$

(P_w = pressure of the wetting fluid ($\text{N} \cdot \text{m}^{-2}$); ρ_{h_2o} = density of water ($\text{kg} \cdot \text{m}^{-3}$); g = gravitational field strength ($\text{N} \cdot \text{kg}^{-1}$); h_w = pressure head of the wetting fluid (m)).

The pressure head of the static wetting fluid can be calculated from

$$h_w = \gamma_w \cdot z_1 \quad (2)$$

where z_1 is the difference in elevation between the PCE overflow and the location of measurement (Figure 14) (m) and is to be taken negative for overflow levels below the point of measurement; γ is the specific gravity (-).

Upon completion of the drainage and imbibition cycles with the air-PCE combination, a 1.5 cm deionized water layer was maintained on top of the sand column to displace the PCE and vice versa (Figure 14). The water was placed on top of the denser and less viscous PCE to minimize fingering during the displacement procedures. The h_c - S imbibition and drainage curves for the PCE-water system were determined in a similar manner as described for the PCE-air. PCE is now the nonwetting

fluid. The wetting and drainage cycles were repeated several times in order to determine the difference between initial and subsequent retention curves.

The capillary pressure head (h_c) for the water-PCE system is calculated according to:

$$h_c = h_{nw} - h_w = \frac{P_{nw} - P_w}{\rho_{h_2o} * g} \quad (3)$$

(P_{nw} = pressure of nonwetting fluid ($N*m^{-2}$); h_{nw} = pressure head of the nonwetting fluid (m)).

Under the assumption that both fluid phases are continuous the pressure head of both static fluids can be calculated from

$$h_w = \gamma_w * z_2 \quad (4)$$

and

$$h_{nw} = \gamma_{nw} * z_1 \quad (5)$$

(z_2 is the vertical distance from the ponded water surface to the point of measurement (Figure 14); γ_{nw} = specific gravity of the nonwetting fluid.)

The calculations of the capillary pressure head, as described above, are only valid if both fluids are continuous. The nonwetting fluid is known to become discontinuous at low values for the capillary pressure head. Since the pressure head of the discontinuous fluids cannot be determined, we calculated the capillary pressure heads as if both fluids were continuous for all saturations.

The h_c -S data were fitted with the closed form van Genuchten expression (1979):

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = [1 + (\alpha * h_c)^n]^{-m} \quad (6)$$

where α (m^{-1}), m and n are curve fitting parameters ($m = 1 - 1/n$), θ_s and θ_r are the saturated and residual volumetric fluid content, respectively, and S_e is the effective saturation (-).

C. RESULTS AND DISCUSSION

Values for the bulk density, porosity and saturated PCE content are given in Table 13. The data indicate that the column was packed reasonably uniformly. It should be noted that about 0.06/0.37 or 16% of the total pore space in the PCE "saturated" column was occupied by entrapped air.

The PCE-air displacement curves were determined for Locations 6, 7, 8, 9 and 10. The results of the van Genuchten curve fitting procedure are shown in Table 14. The air-entry capillary pressure head ($1/\alpha$) is about 9 cm of water and the residual PCE content is about 0.03.

TABLE 14. PARAMETERS FOR THE VAN GENUCHTEN LIQUID RETENTION EQUATION FOR THE PCE DRAINAGE CURVE (VS AIR) FOLLOWED BY THE PCE IMBIBITION CURVE (VS AIR) IN A 1-m LONG COLUMN FILLED WITH FLINTSHOT 2.8 OTTAWA SAND.

Location	θ_r	θ_s	α (cm ⁻¹)	n
PCE drainage curve (vs air)				
6	0.02991	0.30653	0.11049	7.35657
7	0.03194	0.31088	0.11349	7.31198
8	0.02992	0.31078	0.11661	6.97260
9	0.02887	0.30954	0.11370	6.65595
10	< 0.001	0.31401	0.11373	5.43019
PCE wetting curve (vs air)				
6	0.02531	0.30151	0.17785	5.07461
7	0.02452	0.30264	0.17259	5.05552
8	0.02476	0.30335	0.17282	5.35682
9	0.02590	0.30790	0.17666	5.29331
10	0.02835	0.30634	0.17493	5.76977

The measured data and fitted retention curves for the PCE-air at Location 6 are shown in Figure 15. The plot shows that the volumetric PCE content drops from its maximum to its minimum value in about 9 cm of capillary pressure head difference. The data also show significant hysteresis in the θ - h_c relationship. For the same location a so-called scanning curve for PCE and air is shown in Figure 16. First, the air displaced the PCE and the measured data points are almost on the fitted main drainage curve. Then the PCE displaced the air till the second reversal point is reached where the displacement process is again reversed. The resulting scanning curve forms an almost closed loop inside the fitted main wetting and drainage curves.

PCE-water displacement curves were determined at Locations 6 through 12. A big difference between the primary and the secondary wetting data can be observed when water wets a column which was initially saturated with PCE (Figure 17). During the first imbibition, the water did not displace the PCE until the water pressure was almost equal to the pressure of the PCE (h_c was nearly zero). This means that there was no clear wetting fluid. The secondary wetting data (Figure 17) clearly shows water as the wetting fluid for a water-PCE system. Apparently, the water cannot easily displace the adsorbed PCE molecules, unless the water has infiltrated the pores due to pressure gradients. The data points in Figure 17 also clearly show that imbibition and drainage curves do not

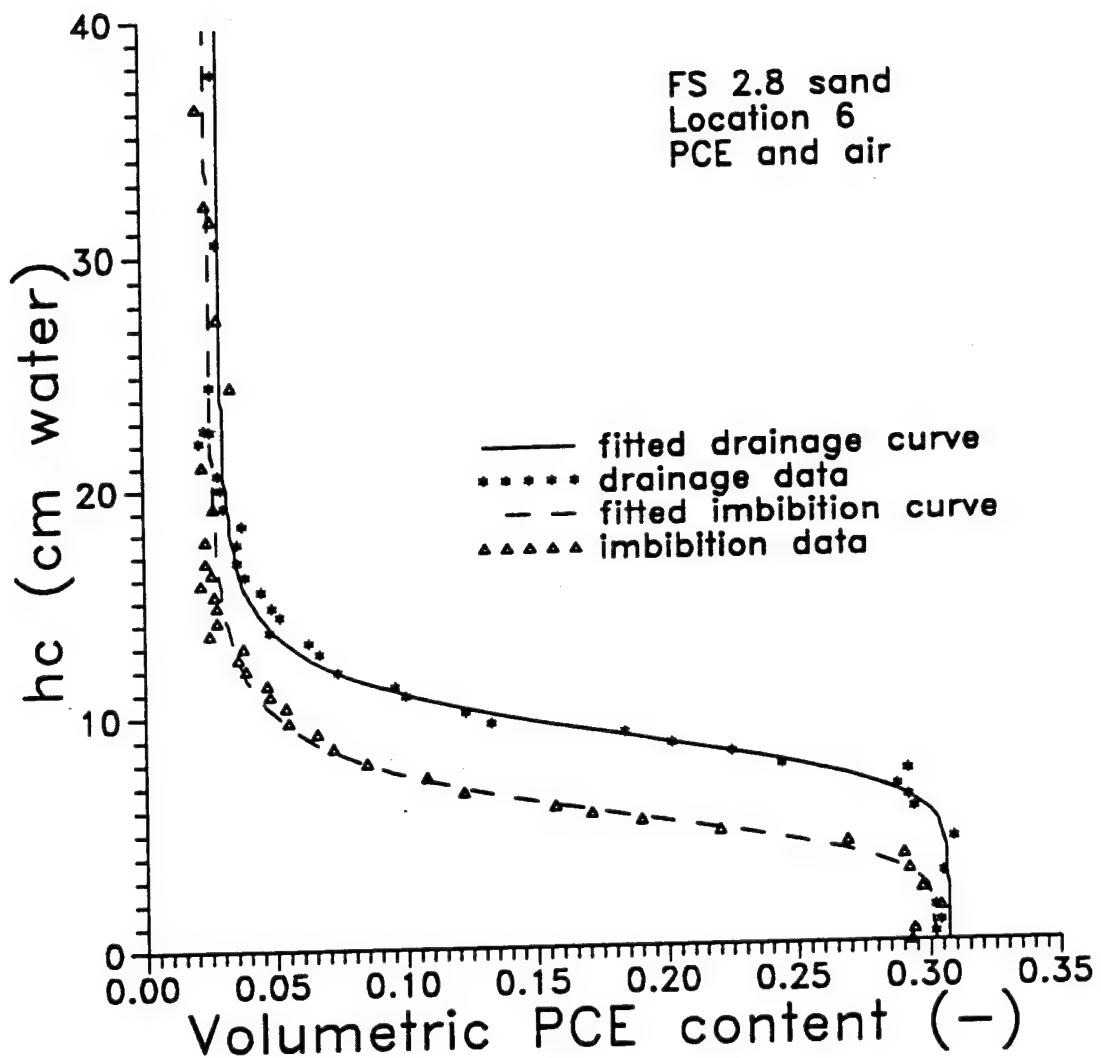


Figure 15. PCE Drainage and Imbibition Curves and Data at Location 6 for a Flintshot 2.8 Ottawa Sand Containing PCE and Air.

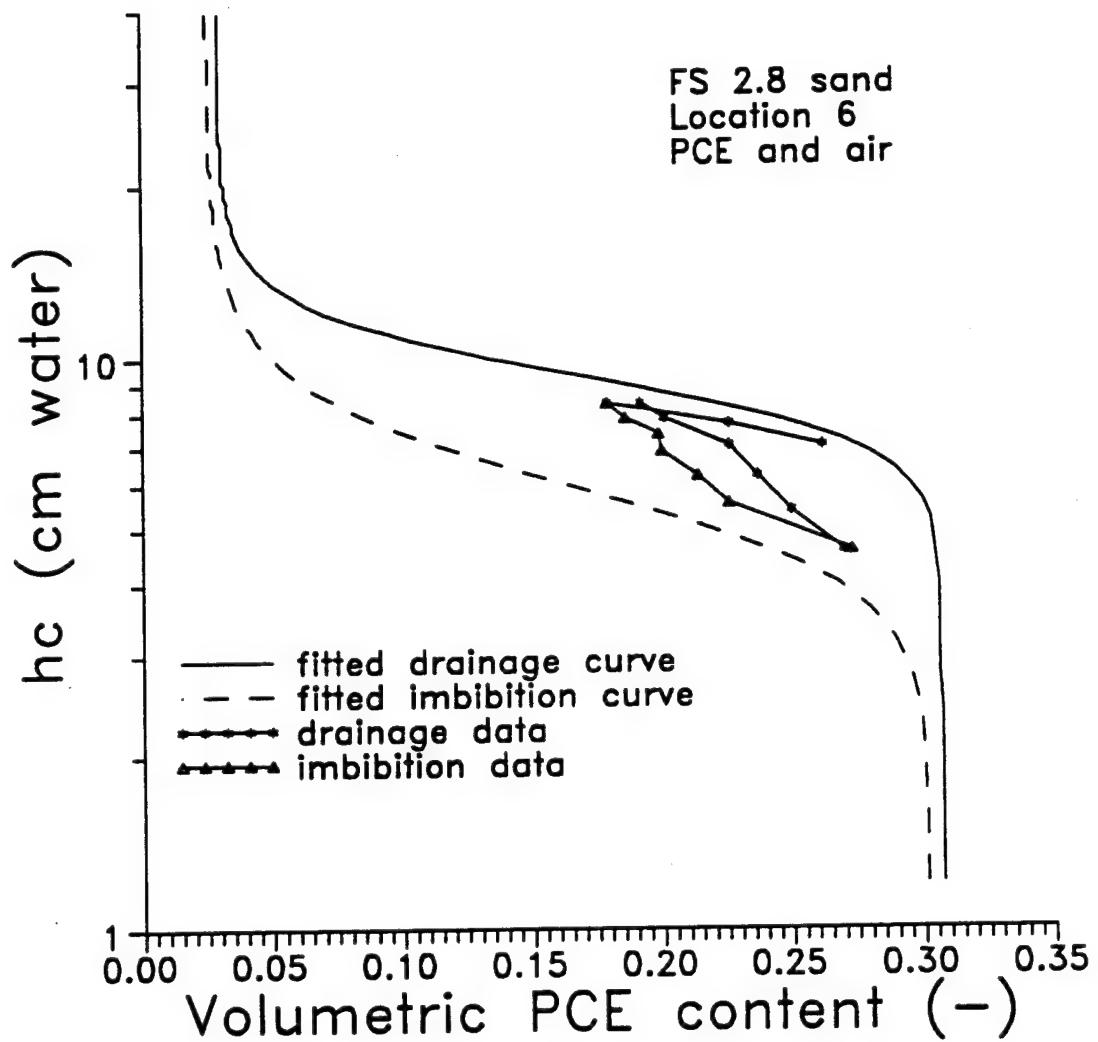


Figure 16. Measured Scanning Path at Location 6 for a Flintshot 2.8 Ottawa Sand Containing PCE and Air.

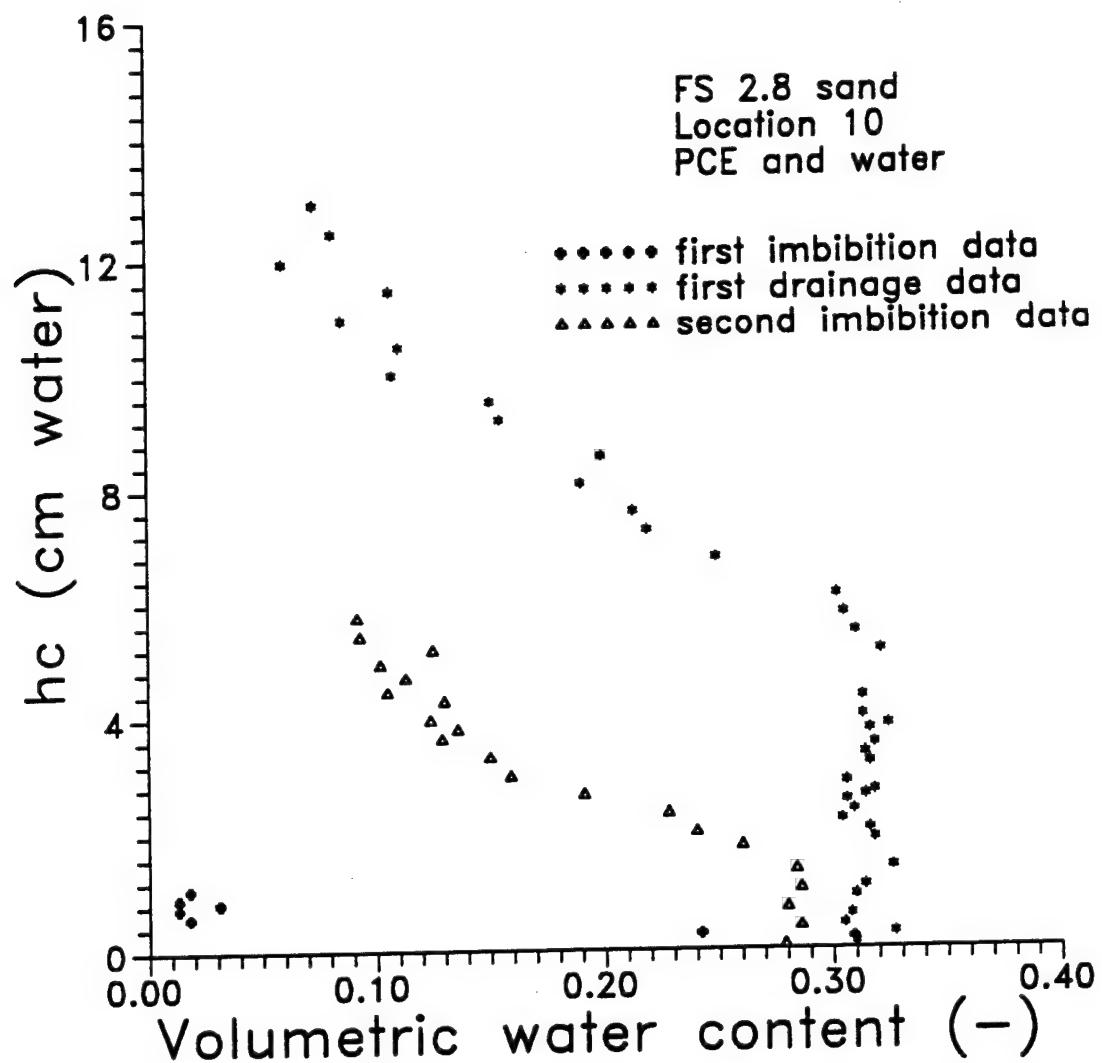


Figure 17. Primary Imbibition and Drainage Data and Secondary Imbibition Data at Location 10 for a Flintshot 2.8 Ottawa Sand Containing Water and PCE.

close at higher saturation of the wetting fluid. This is due to entrapment of the nonwetting fluid during imbibition of the wetting fluid.

Figure 18 shows that tertiary retention curves for water-PCE almost close at Location 12. The water content drops from its maximum value to the residual water content in about 4 cm of head difference.

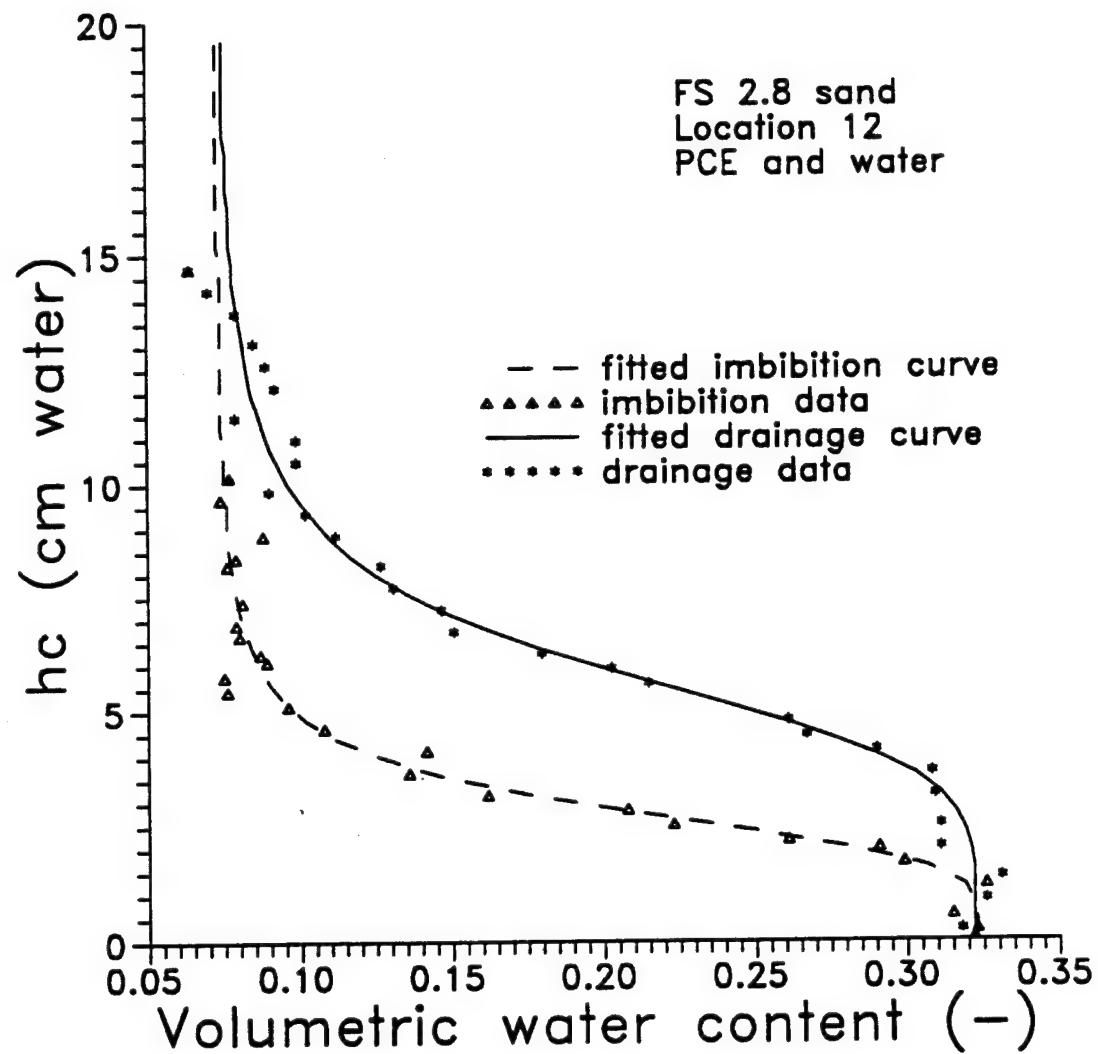


Figure 18. Tertiary Water Drainage and Imbibition Curves and Data at Location 12 for a Flintshot 2.8 Ottawa Sand Containing Water and PCE.

The van Genuchten curve fitting parameters for Location 12 are shown in Table 15. The entry capillary pressure head of PCE is about 6 cm of water. We could not determine complete retention curves for Locations 6-11, because the distance between these points and the surface of the sand was not long enough to obtain θ_r . A scanning curve was determined at Location 12 (Figure 19).

TABLE 15. PARAMETERS FOR THE VAN GENUCHTEN LIQUID RETENTION EQUATION FOR THE WATER DRAINAGE CURVE (VS PCE) FOLLOWED BY THE WATER IMBIBITION CURVE (VS PCE) IN A 1-m LONG COLUMN FILLED WITH FLINTSHOT 2.8 OTTAWA SAND.

Location	θ_r	θ_s	α cm ⁻¹	n
12	0.073	water drainage curve (vs PCE) 0.322	0.178	5.06
12	0.073	water wetting curve (vs PCE) 0.323	0.370	4.63

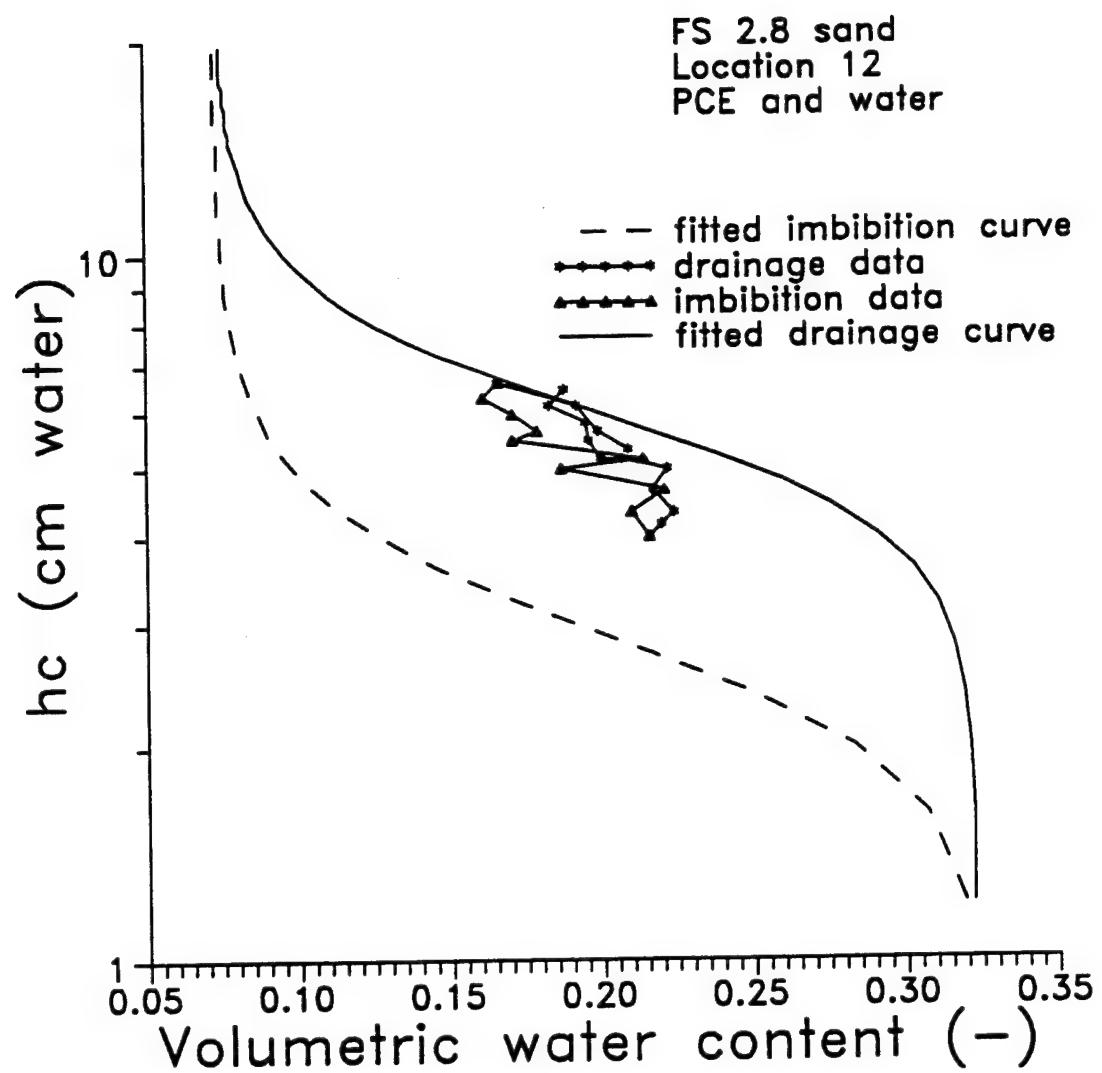


Figure 19. Measured Scanning Path at Location 12 for a Flintshot 2.8 Ottawa Sand Containing Water and PCE.

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SECTION VII

EXPERIMENTAL SETUP FOR TWO-DIMENSIONAL (2-D) FLOW CONTAINER EXPERIMENTS

A. INTRODUCTION

This section provides an overview of the current status of the experimental setup for the two-dimensional(2-D) experiments to be conducted in a flow container. It also describes the experimental setup and the flow container, and its salient features of construction.

B. STATUS OF THE EXPERIMENTAL SETUP FOR THE TWO-DIMENSIONAL EXPERIMENTS

The construction of the flow container, and its supporting steel frame has been completed. Work on the other parts of the experimental setup is underway. Work is continuing on the construction of a fume hood, ducting, and an exhaust stack (Figures 20 and 21) for the experimental setup which will be located in the new Auburn University Subsurface Restoration Laboratory in Room 200 of the Nuclear Science Center. The installation of the fume hood and stack, and the necessary water connections, plumbing, deionized water supply, pumps, and constant head tanks for the flow container are expected to be completed by the end of August 1994.

C. FLOW CONTAINER

The flow container which will be used to conduct the 2-D experiments consists of two inlet and outlet end chambers and a middle porous medium chamber as shown in Figures 22, 23, and 24. The dimensions of the porous medium chamber are 80 cm long, 40 cm high and 10 cm wide. The inlet and outlet end chambers are connected to constant head tanks so that a horizontal ambient flow can be established in the porous medium.

The container is made of Teflon®, glass and stainless steel materials which do not react with the chemicals to be used in the experiments such as perchloroethylene (PCE) and quadricyclane. The front of the porous medium chamber is made of glass to allow visualization and to be able to take photographs during the experiments. The teflon parts are etched and then put together using a chemgrip bonding kit (Ain Plastics, Norfolk, VA). The pieces are also screwed together for extra strength. The joints are then sealed using a solvent resistant sealant (DOW Corning, Midland, MI) to prevent any leaks. The sealant is resistant to PCE and most solvents. The flow container also has a steel frame around it (as shown in Figure 25) to support it and to prevent it from undergoing excessive deflection. A photograph of the flow container is shown in Figure 26.

The inlet and outlet end chambers and the porous medium chamber are separated by filters made of perforated teflon sheets with a stainless steel wire cloth (McMaster Carr Co., Atlanta, GA) in between. The wire cloth prevents the porous medium particles from passing through the filters into the end chambers. The inlet and outlet end chambers are provided with piezometric tubes in order to observe the levels (head) of water at both ends. The porous medium chamber will be packed with a

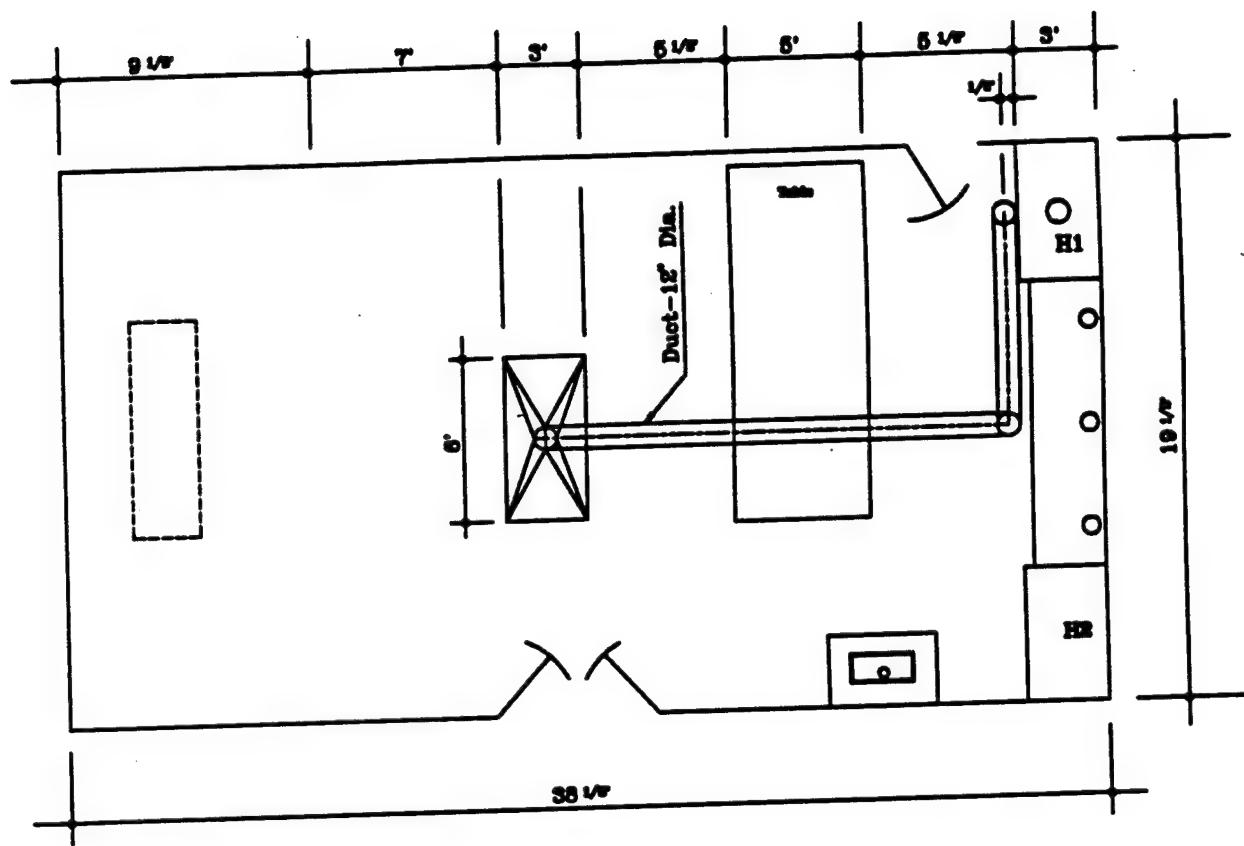


Figure 20. Plan View of the Subsurface Restoration Laboratory
(Room 200, Nuclear Science Center).

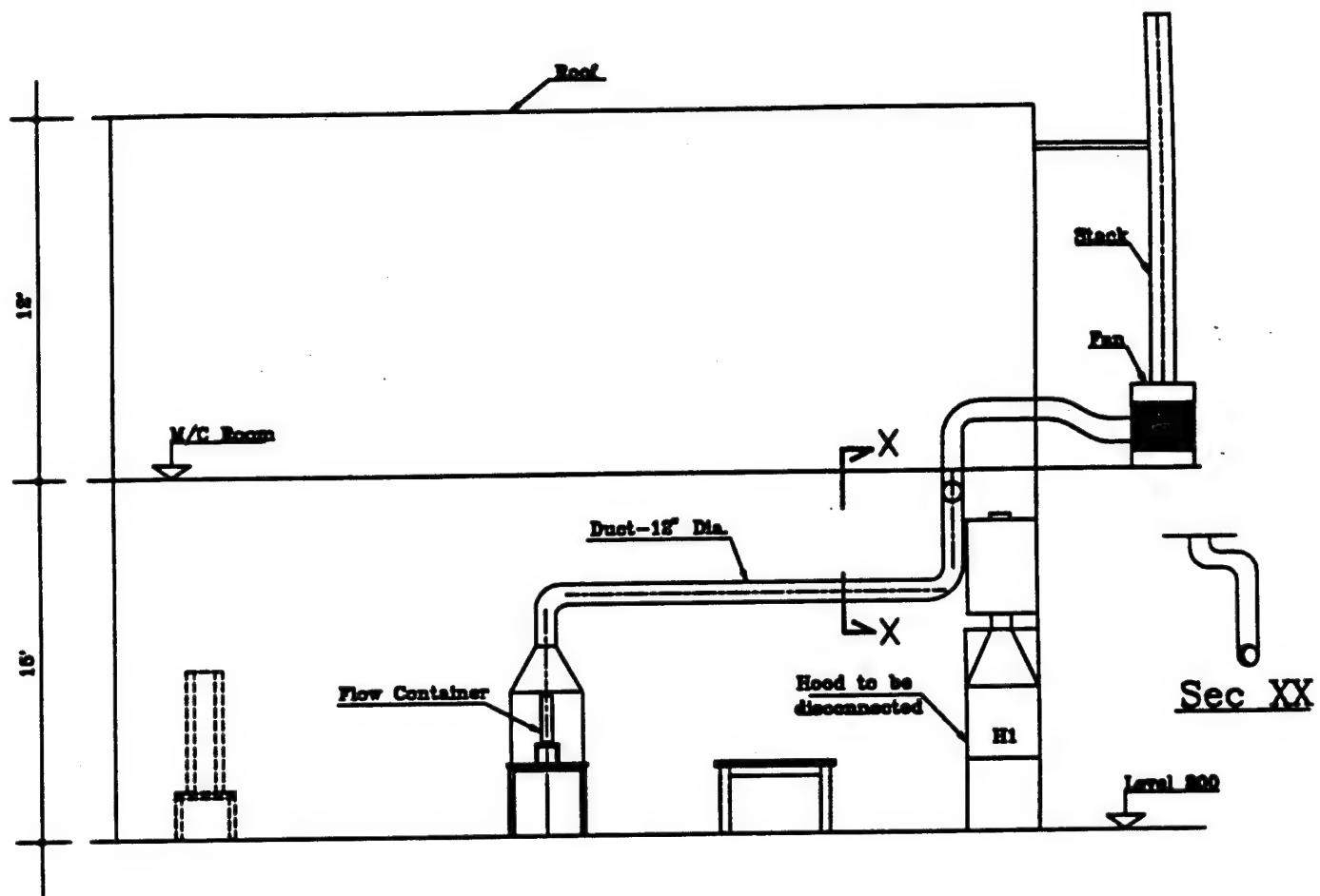


Figure 21. Elevation View of the Fume Hood, Ducting, and Stack.

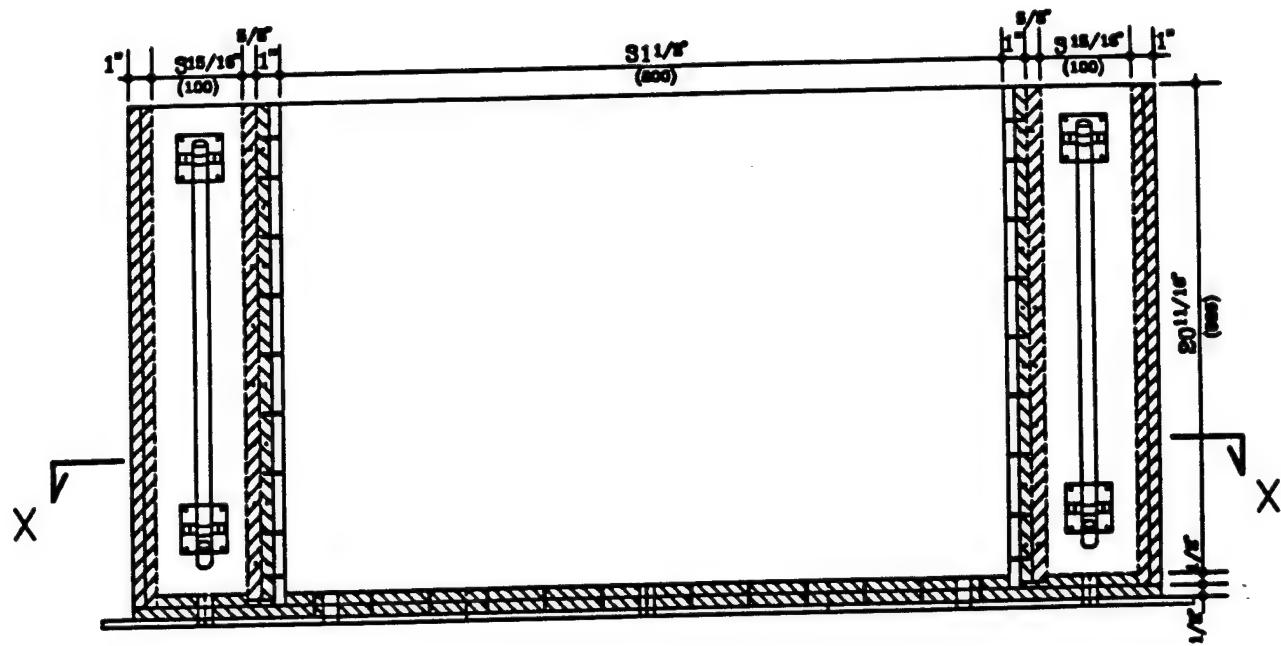


Figure 22. Front Elevation View of the Flow Container.

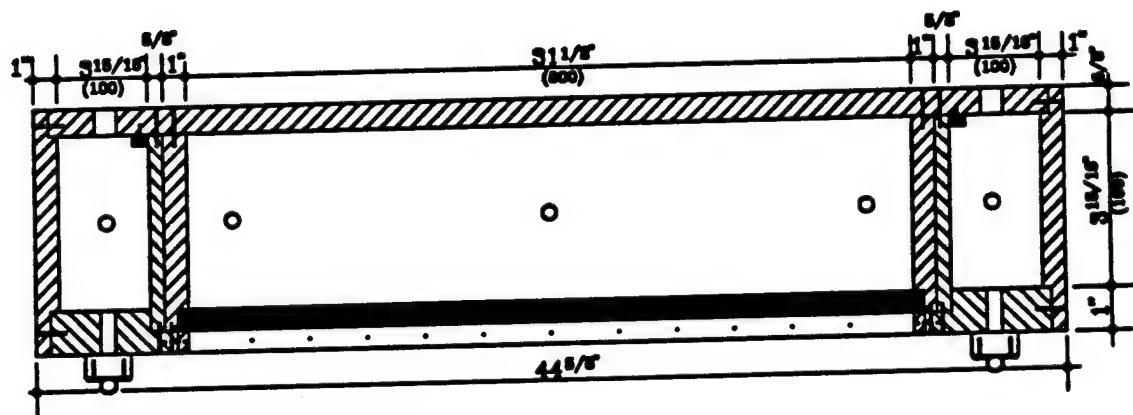


Figure 23. Section X-X (Figure 22) of the Flow Container.

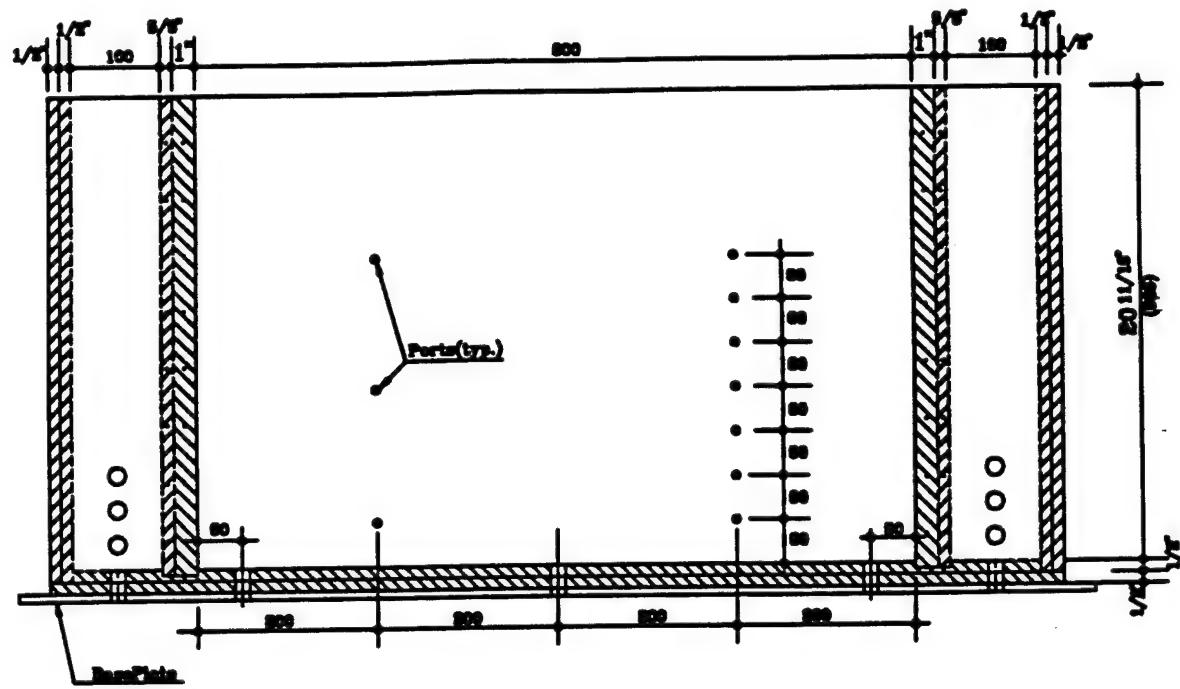


Figure 24. Back Elevation View of the Flow Container.

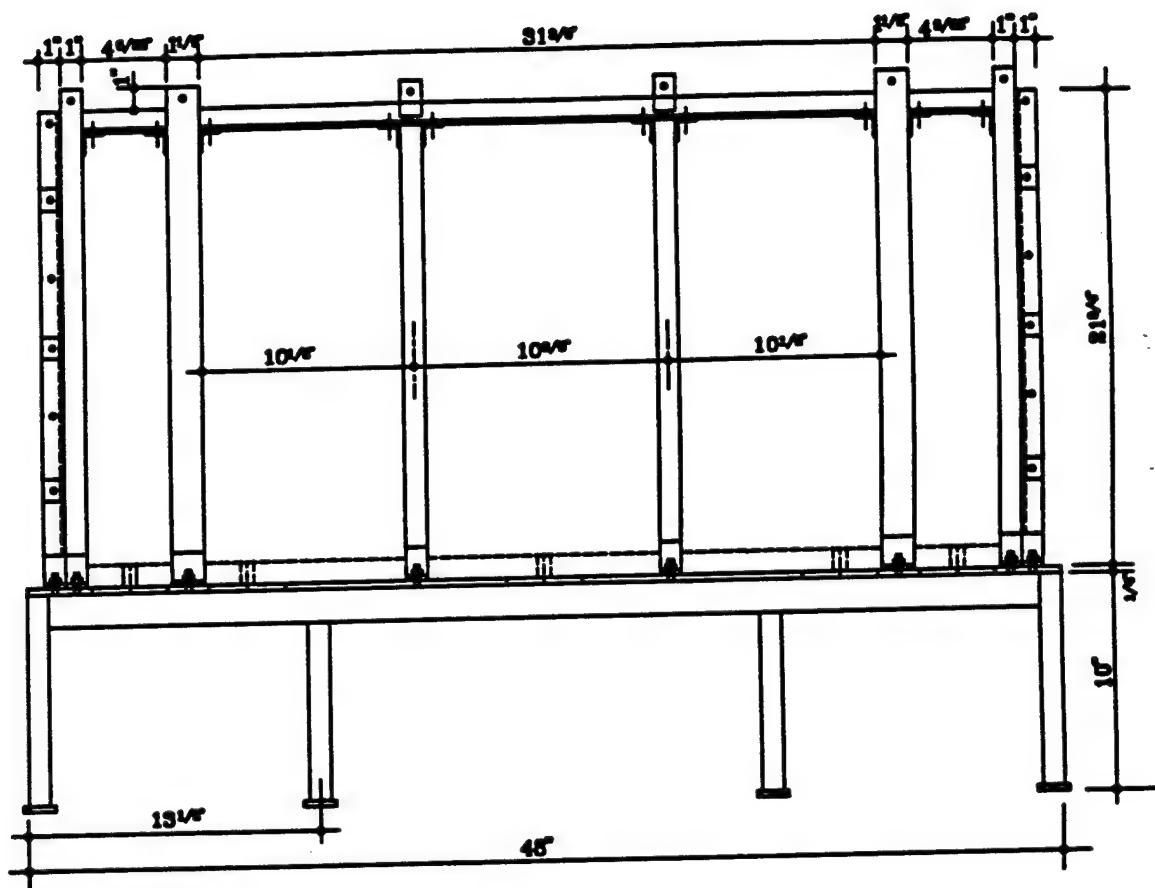


Figure 25. Elevation View of the Flow Container with the Supporting Steel Frame.

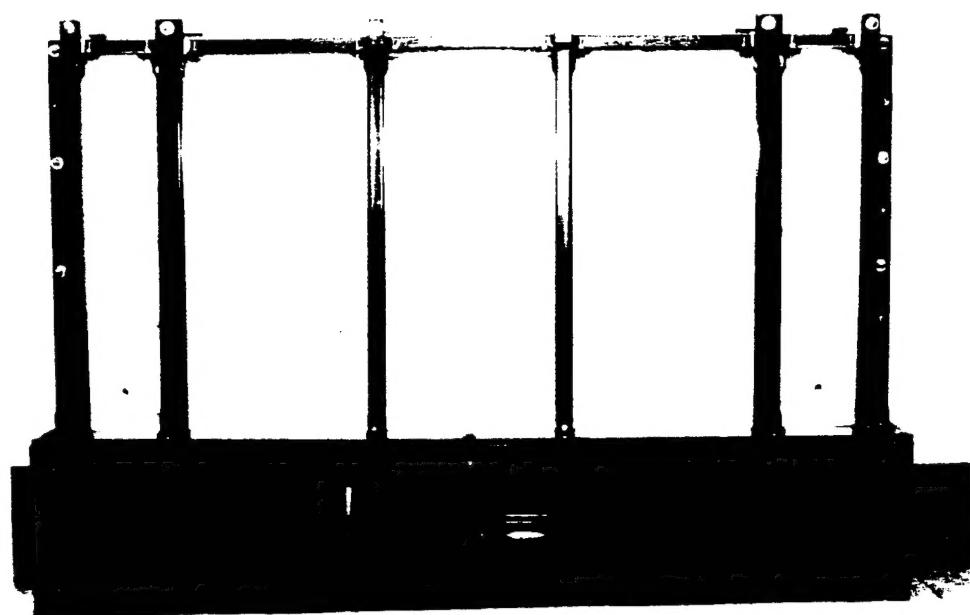


Figure 26. Photograph of the Front of the Flow Container.

nominally homogenous porous medium composed of glass beads (e.g., Potters Industries, series A-120) or clean uniform sand (e.g., Flintshot 2.8 Ottawa Sand).

The porous medium chamber is provided with ten injection and extraction ports through which fluids can be injected and extracted (see Figure 24). Each port is made of a stainless steel tube 1/4" in diameter with 3/64" diameter holes drilled around it at uniform spacing and staggered so as to cause the fluid to be injected or extracted to flow uniformly in all directions. A photograph of an injection and extraction port is shown in Figure 27.

In this study we will deal with the migration and redistribution of nonaqueous phase liquids (NAPLs) in the porous medium. The NAPLs to be studied are perchloroethylene (a DNAPL, with a specific gravity of 1.63) and quadricyclane (a LNAPL, with a specific gravity of 0.92). In the 2-D flow container experiments known amounts of the NAPL will be introduced in a stepwise manner into the porous medium through a line source. The subsequent movement of the NAPL will be monitored and recorded by taking flow visualization photographs. The injection and extraction of fluids through the ports will be done using peristaltic pumps. These ports will allow us to create vertically and horizontally circulating flow fields in some of the experiments.

D. FUME HOOD, DUCTING, AND STACK

A fume hood, ducts, and an exhaust stack are being constructed (Figures 20 and 21) for the experimental setup in order to prevent the harmful vapors of the NAPLs from accumulating in the laboratory. A 10-foot high stack will also be constructed on the top of the building so that the vapors do not reenter the building and to ensure adequate mixing. The fume hood is to have a face velocity (air flow velocity) of 100 feet per minute as required by the current safety and environmental standards.

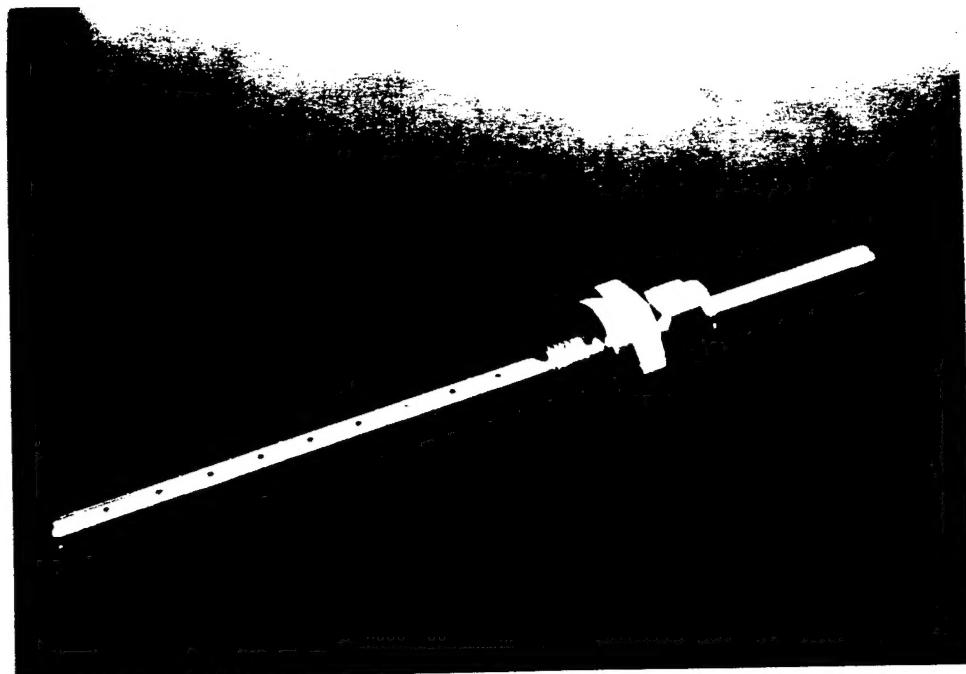


Figure 27. Photograph of an Injection and Extraction Port.

SECTION VIII CONCLUSIONS

This report describes the work performed during the first year of this project. The project is on schedule and there are no current or anticipated problems. All the tasks planned for the first year have been completed, and the preparatory work necessary for the initiation and performance of the remaining tasks has been either completed or is very close to completion. During the second year, work will be initiated on the planned 2-D transport experiments with quadricyclane and PCE (namely, Tasks 1.5 and 2.4). In addition, work will continue on additional batch and 1-D transport experiments with quadricyclane and test soils (Task 1.4), and on additional 1-D transport experiments with PCE with heterogeneous porous media (Task 2.3).